Supporting Information

ansa-Metallocene Based Cyclic[2]pyrroles:

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Synthesis of 6:

1, 1'-Bis (diphenylhydroxymethyl)ferrocene (**1**) (1.5 g, 2.73 mmol) and pyrrole (7.6 ml, 109.1 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.04 ml, 0.273 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. The product was filtered and thoroughly washed with pet ether to remove excess pyrrole and yellow residue was identified as **6**. Yield: 80% (1.42 g); m.p: 230˚ C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (brs, 2H, pyrrole NH), 7.19-7.14 (m, 12H, phenyl CH), 6.95-6.92 (m, 8H, phenyl CH), 6.69 (s, 2H, α-pyrrole CH), 6.10 (q, 2H, β-pyrrole CH), 5.75 (s, 2H, β-pyrrole CH), 3.88 (s, 4H, ferrocenyl CH), 3.74 (s, 4H, ferrocenyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 54.70, 70.61, 70.85, 97.48, 108.03, 108.47, 109.98, 116.44, 117.98, 126.85, 127.65, 129.64, 136.64, 148.00; FT-IR (CH_2Cl_2) 3428.57, 2917.58, 1637.87, 1486.99, 1262.03, 1019.20 cm^{-1}; FAB-MS (m/z): 648.

Synthesis of 7:

1, 1'-Bis (methyl-phenylhydroxymethyl)ferrocene (**2**) (0.5 g, 1.2 mmol) and pyrrole (3.3 ml, 47 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.015 ml, 0.12 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. The work up was done using NaOH solution, water and the organic layer was extracted with dichloromethane and dried over anhydrous sodium sulphate. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with

ethyl acetate: petroleum ether (3 : 97) gave a pale yellow solid identified as **7**. Yield: 65% (0.4 g); m.p: 164˚ C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (brs, 2H, pyrrole NH), 7.18 (m, 10H, phenyl CH), 6.99 (m, 4H, phenyl CH), 6.61 (s, 2H, α-pyrrole CH), 6.13 (t, 2H, β-pyrrole CH), 5.96 (s, 2H, β-pyrrole CH), 3.99 (s, 4H, ferrocenyl CH), 3.90 (t, 3H, ferrocenyl CH), 3.82 (s, 1H, ferrocenyl CH), 1.94 (s, 6H, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 28.77, 43.29, 68.30, 68.35, 68.41, 68.47, 68.86, 69.02, 98.12, 105.66, 107.46, 115.99, 126.09, 139.64, 148.80; FT-IR (CH_2Cl_2) 3436.18, 2979.86, 1593.98, 1492.47, 1444.84, 1366.28, 1265.28, 1025.07 cm^{-1}; FAB-MS (m/z): 524.06.

Synthesis of 8:

1, 1'-Bis(cyclohexylhydroxymethyl)ferrocene (**3**) (0.8 g, 2.1 mmol) and pyrrole (5.8 ml, 84 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.03 ml, 0.21 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with ethyl acetate : petroleum ether (3.5 : 96.5) gave a pale yellow solid identified as **8**. Yield: 80% (0.8 g); m.p: 145˚ C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93 (brs, 2H, pyrrole NH), 6.67 (s, 2H, α-pyrrole CH), 6.15 (d, J = 2.73 Hz, 2H, β-pyrrole CH), 6.02 (s, 2H, β-pyrrole CH), 3.97 (s, 4H, ferrocenyl CH), 3.84 (s, 4H, ferrocenyl CH), 2.23 (d, J : 13.3 Hz, 4H, cyclohexyl CH), 1.77 (m, 5H, cyclohexyl CH), 1.42 (m, 6H, cyclohexyl CH), 1.23 (m, 3H, cyclohexyl CH), 0.88 (m, 2H, cyclohexyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 22.46, 22.86, 23.45, 26.75, 27.85, 28.45, 29.50, 35.15, 36.17, 38.26, 42.57,

64.75, 65.17, 67.17, 68.19, 69.15, 128.45, 137.75, 147.56; FT-IR (CH_2Cl_2) 3428.94, 3093.40, 2929.48, 1591.23, 1443.09, 1264.77, 1031.13 cm^{-1}; FAB-MS (m/z): 480.75.

Synthesis of 9:

1, 1'-Bis(diethylhydroxymethyl)ferrocene (**4**) (0.8 g, 2.2 mmol) and pyrrole (6.2 ml, 88.8 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.03 ml, 0.22 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with ethyl acetate: petroleum ether (3.5 : 96.5) gave a pale yellow solid identified as **9**. Yield: 68% (0.679 g); m.p: 122° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.97 (brs, 2H, pyrrole NH), 6.74 (s, 2H, α-pyrrole CH), 6.17 (d, J : 2.45 Hz, 2H, β-pyrrole CH), 6.02 (s, 2H, β-pyrrole CH), 4.15 (s, 4H, ferrocenyl CH), 3.93 (s, 4H, ferrocenyl CH) , 1.87 (m, 8H, ethyl CH), 0.7 (t, 12H, ethyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 9.21, 32.07, 41.99, 67.92, 68.68, 106.28, 107.45, 115.86, 136.31; FT-IR (CH_2Cl_2) 3426.77, 3097.84, 2967.48, 2877.34, 1556.44, 1463.89, 1082.47, 1036.45, 827.36, 786.10 cm^{-1}; FAB-MS (m/z): 456.74.

Synthesis of 10:

1, 1'-Bis(dimethylhydroxymethyl)ferrocene (**5**) (0.88 g, 2.91 mmol) and pyrrole (8 ml, 116.6 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.04 ml, 0.291 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction

eluted with ethyl acetate : petroleum ether (3 : 97) gave a pale yellow solid identified as **10**. Yield: 65% (0.76 g); m.p: 108° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76 (brs, 2H, pyrrole NH), 6.48 (q, 2H, α-pyrrole CH), 6.01 (q, 2H, β-pyrrole CH), 5.85 (s, 2H, β-pyrrole CH), 4.09 (s, 4H, ferrocenyl CH), 4.02 (s, 4H, ferrocenyl CH), 1.56 (s, 12H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 29.98, 34.24, 68.25, 68.32, 99.37, 102.71, 107.77, 115.57, 140.86; FT-IR (CH_2Cl_2) 3417.58, 2917.58, 1594.01, 1262.03, 1119.38, 1023.36 cm^{-1}; FAB-MS (m/z): 400.18.

Synthesis of 24:

1, 1'-Bis(diphenylhydroxymethyl)ruthenocene (**23**) (1 g, 1.7 mmol) and pyrrole (5 ml, 68 mmol) were stirred under nitrogen atmosphere for 10 min at room temperature. $BF_3.OEt_2$ (0.02 ml, 0.17 mmol) was added to the above mixture and the solution was stirred at room temperature for further 1h under dark conditions. Then it is quenched with 75 ml dichloromethane. The product was filtered and thoroughly washed with pet ether to remove excess pyrrole and white residue was identified as **24**. Yield: 81% (0.95 g); m.p: 194° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.23 (brs, 2H, pyrrole NH), 7.21 (m, 12H, phenyl CH), 7.01 (m, 8H, phenyl CH), 6.70 (t, 2H, α-pyrrole CH), 6.10 (t, 2H, β-pyrrole CH), 5.58 (t, 2H, β-pyrrole CH), 4.39 (s, 4H, ferrocenyl CH), 4.24 (s, 4H, ferrocenyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 73.66, 74.27, 100.76, 107.54, 109.51, 115.81, 126.45, 127.24, 129.23, 147.89; FT-IR (CH_2Cl_2) 3433.77, 2923.07, 1593.98, 1259.29, 1116.63, 1027.70 cm^{-1}; FAB-MS (m/z): 694.10.

Synthesis of 11:

6 (0.5 g, 0.77 mmol) and acetone (60 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.006 ml, 0.077 mmol) was added

to the above mixture and the solution was stirred at room temperature for 2 days. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **11**. Yield: 48 % (0.26 g); m.p: 145° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.24 (brs, 2H, pyrrole NH), 7.31 (m, 16H, phenyl CH), 6.58 (d, J = 9.2 Hz, 4H, phenyl CH), 6.02 (s, 2H, β-pyrrole CH), 5.07 (s, 2H, β-pyrrole CH), 4.10 (d, J = 11.8 Hz, 4H, ferrocenyl CH), 2.94 (s, 2H, ferrocenyl CH), 2.81 (s, 2H, ferrocenyl CH), 1.79 (s, 6H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 29.29, 33.45, 42.45, 55.80, 66.5, 71.80, 72.45, 99.58, 110.04, 111.57, 112.19, 119.55, 119.78, 124.76, 128.76, 130.75, 135.78; FT-IR (CH_2Cl_2) 3431.36, 3065.93, 2924.00, 2853.25, 1597.45, 1492.09, 1443.09, 1415.66, 1275.75, 1220.88, 1048.43, 842.30 cm^{-1}; FAB-MS (m/z): 689.11.

The above macrocycle was also be obtained by the following method. **1** (0.2 g, 0.36 mmol) and **19** (0.063 g, 0.36 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.017 g, 0.09 mmol) were added to the above reaction mixture and allowed to stir for 2 days. Then the purification was done as above.

Synthesis of 12:

7 (0.26 g, 0.5 mmol) and acetone (37 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.004 ml, 0.05 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate :

petroleum ether (1 : 99) gave a pale yellow solid identified as **12**.Yield: 19% (0.05 g); m.p: 140° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.75 (brs, 2H, pyrrole NH), 7.13 (d, J = 6.765 Hz, 6H, phenyl CH), 6.90 (d, J = 7.836 Hz, 4H, phenyl CH), 5.96 (t, 2H, β-pyrrole CH), 5.46 (t, 2H, β-pyrrole CH), 4.25 (s, 4H, ferrocenyl CH), 4.17 (s, 2H, ferrocenyl CH), 3.18 (s, 2H, ferrocenyl CH), 1.97 (s, 6H, methyl CH), 1.65 (s, 6H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 27.45, 29.47, 34.5, 41.5, 68.40, 68.69, 69.45, 69.76, 70.15, 99.15, 106.70, 107.05, 113.25, 127.11, 138.75; FT-IR (CH_2Cl_2) 3428.57, 3313.18, 2917.58, 2851.64, 1596.43, 1445.84, 1119.38, 1086.46 cm^{-1}; FAB-MS (m/z): 564.37.

The above macrocycle was also be obtained by the following method.**2** (0.2 g, 0.47 mmol) and **19** (0.082 g, 0.47 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.022 g, 0.12 mmol) were added to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 13:

8 (0.2 g, 0.42 mmol) and acetone (31 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.003 ml, 0.042 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **13**. Yield: 22% (0.047g); m.p: 123° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70 (brs, 2H, pyrrole NH), 6.12 (t, 2H, β-pyrrole CH), 5.88 (q, 2H, β-pyrrole CH), 4.06 (m, 6H, ferrocenyl CH), 2.86 (d, J = 0.897 Hz, 2H, ferrocenyl CH), 2.15 (m, 5H, cyclohexyl CH), 1.74 (m, 5H, cyclohexyl CH), 1.6

(s, 6H, methyl CH), 1.38 (m, 6H, cyclohexyl CH), 0.87 (m, 4H, cyclohexyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 21.15, 22.75, 23.16, 26.79, 28.95, 29.05, 29.75, 36.15, 36.27, 39.45, 42.75, 65.66, 66.17, 67.18, 68.25, 69.16, 127.15, 138.45; FT-IR (CH_2Cl_2) 3456.04, 3093.40, 2925.44, 2854.50, 1574.77, 1446.97, 1415.66, 1264.77, 1187.96, 1042.56, 930.08 cm^{-1}; FAB-MS (m/z): 520.33.

The above macrocycle was also be obtained by the following method.**3** (0.2 g, 0.52 mmol) and **19** (0.091 g, 0.52 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.025 g, 0.13 mmol) were added to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 14:

9 (0.45 g, 1 mmol) and acetone (73 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.007 ml, 0.1 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **14**.Yield: 19% (0.094 g); m.p: 120° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.23 (brs, 2H, pyrrole NH), 6.06 (t, 2H, β-pyrrole CH), 5.90 (t, 2H, β-pyrrole CH), 4.19 (d, J = 1.164 Hz, 2H, ferrocenyl CH), 4.10 (m, 4H, ferrocenyl CH), 3.02 (s, 2H, ferrocenyl CH), 1.94 (m, 8H, ethyl CH), 1.66 (s, 6H, methyl CH), 0.79 (t, 6H, ethyl CH), 0.71 (t, 6H, ethyl CH); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 9.18, 30.58, 31.51, 33.45, 36.23, 41.24, 65.57, 66.45, 67.45, 69.34, 102.59, 103.20,

105.84, 134.62, 136.94; FT-IR (CH_2Cl_2) 3434.06, 3329.67, 2922.90, 2851.64, 1742.12, 1585.75, 1259.29, 1119.38, 1018.49 cm^{-1}; FAB-MS (m/z): 496.60.

The above macrocycle was also be obtained by the following method. **4** (0.2 g, 0.56 mmol) and **19** (0.097 g, 0.56 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.027 g, 0.14 mmol) were added to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 15:

10 (0.5 g, 1.25 mmol) and acetone (60 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.01 ml, 0.125 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **15**. Yield: 25% (0.13 g); m.p: 115° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (brs, 2H, pyrrole NH), 6.02 (s, 2H, β-pyrrole CH), 5.82 (s, 2H, β-pyrrole CH), 4.07 (s, 2H, ferrocenyl CH), 3.97 (d, J = 11.3 Hz, 4H), 2.90 (s, 2H, ferrocenyl CH), 1.6 (s, 18H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.56, 26.75, 27.17, 29.15, 35.47, 68.15, 68.42, 98.45, 113.45, 114.55, 126.77, 137.11; FT-IR (CH_2Cl_2) 3457.95, 3087.91, 2924.14, 2854.34, 1651.59, 1580.26, 1463.16, 1377.42, 1259.29, 1041.33, 828.58 cm^{-1}; FAB-MS (m/z): 439.98.

The above macrocycle was also be obtained by the following method.**5** (0.2 g, 0.66 mmol) and **19** (0.12 g, 0.66 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.031 g, 0.17 mmol) were added

to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 16:

7 (0.235 g, 0.45 mmol) and acetophenone (0.05ml, 0.45 mmol) were dissolved in 30 ml dry dichloromethane and stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.003 ml, 0.045 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **16**. Yield: 23% (0.063 g); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.03 (brs, 2H, pyrrole NH), 7.38 (d, J = 6.81 Hz, 8H, phenyl CH), 6.95 (d, J = 6.36 Hz, 3H, phenyl CH), 6.8 (d, J = 6.95 Hz, 4H, phenyl CH), 6.03 (t, 2H, β-pyrrole CH), 5.95 (t, 2H, β-pyrrole CH), 4.03 (s, 4H, ferrocenyl CH), 3.38 (s, 2H, ferrocenyl CH), 3.04 (s, 2H, ferrocenyl CH), 1.91 (s, 9H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.15, 26.17, 27.15, 35.15, 40.17, 66.70, 67.15, 67.45, 68.56, 69.15, 69.98, 98.15, 107.17, 108.05, 114.15, 128.11, 139.34; FT-IR (CH_2Cl_2) 3438.11, 2923.44, 2846.15, 1593.06, 1465.04, 1264.77, 1215.39, 1122.12, 1031.59 cm^{-1}; FAB-MS (m/z): 626.39.

The above macrocycle was also be obtained by the following method.**2** (0.2 g, 0.47 mmol) and **20** (0.11 g, 0.47 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.022 g, 0.12 mmol) were added to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 17:

8 (0.2g, 0.42 mmol) and cyclohexanone (0.04ml, 0.42 mmol) were dissolved in 30 ml dry dichloromethane and stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.003 ml, 0.042 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **17**. Yield: 25% (0.058g); m.p: 205° C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (brs, 2H, pyrrole NH), 6.20 (t, 2H, β-pyrrole CH), 5.87 (t, 2H, β-pyrrole CH), 4.08 (s, 2H, ferrocenyl CH), 4.04 (s, 2H, ferrocenyl CH), 3.99 (s, 2H, ferrocenyl CH), 2.97 (s, 2H, ferrocenyl CH), 2.28 (m, 3H, cyclohexyl CH), 2.08 (t, 6H, cyclohexyl CH), 1.83 (m, 10H, cyclohexyl CH), 1.26 (m, 9H, cyclohexyl CH), 0.88 (m, 2H, cyclohexyl CH); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 22.59, 22.78, 22.95, 23.15, 23.36, 25.94, 26.06, 26.14, 29.67, 37.88, 38.73, 39.01, 39.36, 39.78, 40.29, 40.84, 63.23, 65.10, 65.98, 66.16, 67.09, 68.55, 105.14, 105.32, 105.43, 106.37, 133.85, 136.44; FT-IR (CH_2Cl_2) 3450.54, 2924.11, 2851.64, 1640.61, 1443.09, 1215.39, 1119.38, 1042.56, 930.08 cm^{-1}; FAB-MS (m/z): 560.06.

The above macrocycle was also be obtained by the following method.**3** (0.2 g, 0.52 mmol) and **21** (0.11 g, 0.52 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.025 g, 0.13 mmol) were added to the above reaction mixture and allowed to stir for 45 min. Then the purification was done as above.

Synthesis of 18:

9 (0.2 g, 0.42 mmol) and 3-pentanone (0.05 ml, 0.42 mmol) were dissolved in 30 ml dry dichloromethane and stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.003 ml, 0.042 mmol) was added to the above mixture and the solution was stirred at room temperature for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). A yellow fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **18**. Yield: 17% (0.040g); m.p: 115° C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (brs, 2H, pyrrole NH), 5.98 (t, 2H, β-pyrrole CH), 5.93 (t, 2H, β-pyrrole CH), 4.20 (s, 2H, ferrocenyl CH), 4.09 (d, J = 7.5 Hz, 4H, ferrocenyl CH), 2.99 (s, 2H, ferrocenyl CH), 1.97 (m, 12H, ethyl CH), 0.76 (t, 18 H, ethyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 9.15, 10.15, 15.16, 31.15, 32.41, 35.15, 42.15, 66.78, 67.15, 68.11, 69.15, 104.15, 105.16, 133.15, 135.78; FT-IR (CH_2Cl_2) 3429.52, 3321.25, 2947.16, 1676.87, 1560.08, 1260.00, 1085.15, 1040.87, 819.56 cm^{-1}; FAB-MS (m/z): 524.33.

The above macrocycle was also be obtained by the following method.**4** (0.2 g, 0.56 mmol) and **22** (0.113 g, 0.56 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.026 g, 0.14 mmol) were added to the above reaction mixture and allowed to stir for 45 min Then the purification was done as above.

Synthesis of 25:

24 (0.2 g, 0.29 mmol) and acetone (21 ml) were stirred under nitrogen atmosphere for 10 min at room temperature. Trifluoroacetic acid (0.002 ml, 0.029 mmol) was added to the above mixture and the solution was stirred at room temperature for 2 days. After

removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). The colourless fraction eluted with Ethyl acetate : petroleum ether (1 : 99) gave a pale yellow solid identified as **25**. Yield: 23.5 % (0.05 g); m.p: 135° C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.86 (brs, 2H, pyrrole NH), 7.31 (m, 16H, phenyl CH), 6.91 (m, 4H, phenyl CH), 5.96 (t, 2H, β-pyrrole CH), 5.17 (t, 2H, β-pyrrole CH), 4.44 (s, 2H, ferrocenyl CH), 4.38 (s, 2H, ferrocenyl CH), 3.66 (s, 2H, ferrocenyl CH), 3.43 (s, 2H, ferrocenyl CH); 1.72 (s, 6H, methyl CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.45, 26.17, 28.17, 42.35, 69.15, 71.15, 72.46, 100.15, 108.91, 116.45, 127.15, 136.15; FT-IR (CH_2Cl_2) 3372.49, 3049.45, 2920.67, 2846.15, 1596.87, 1486.99, 1443.09, 1273.00, 1217.96, 1037.07, 814.86 cm^{-1}; FAB-MS (m/z): 734.22.

The above macrocycle was also be obtained by the following method.**23** (0.2 g, 0.34 mmol) and **19** (0.059 g, 0.34 mmol) were allowed to stir under nitrogen atmosphere in 30 ml dry dichloromethane for 10 min. Then *p*-TSA (0.016 g, 0.09 mmol) were added to the above reaction mixture and allowed to stir for 2 days. Then the purification was done as above.

Figure – 1: Mass Spectrum of **6**

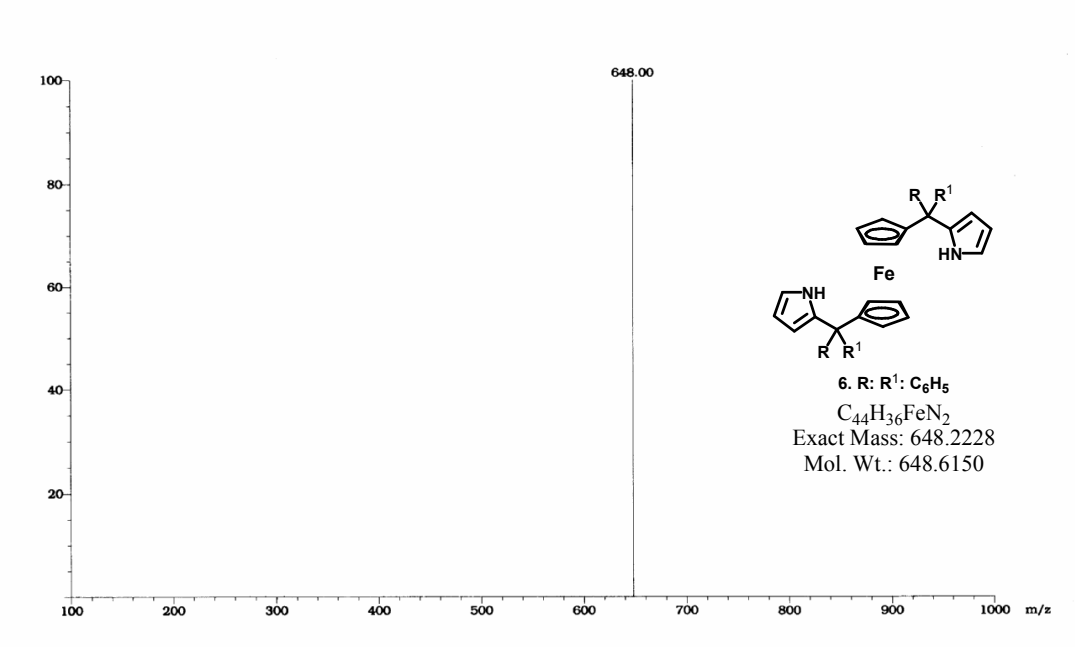


Figure – 1: Mass Spectrum of **7**

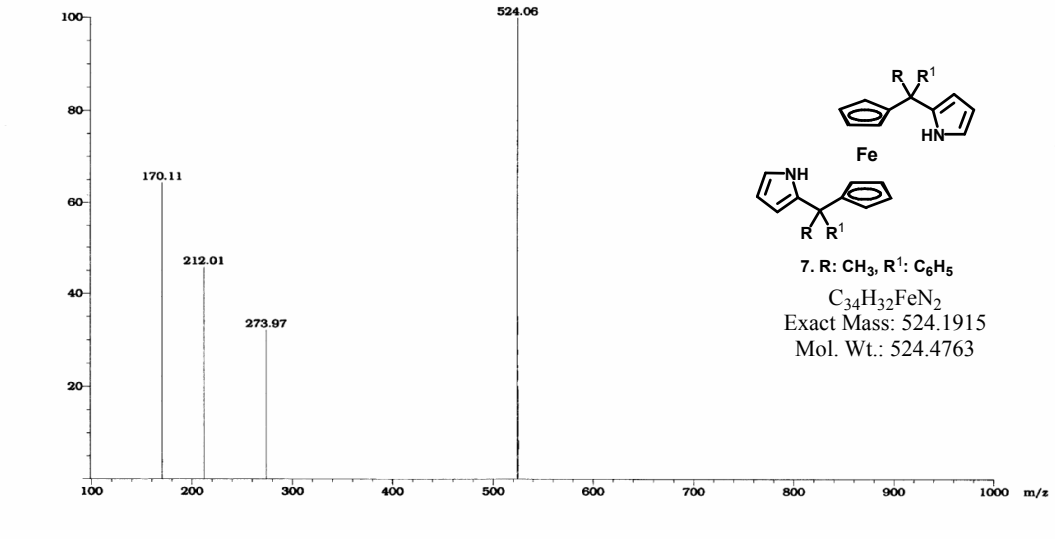


Figure – 1: Mass Spectrum of **8**

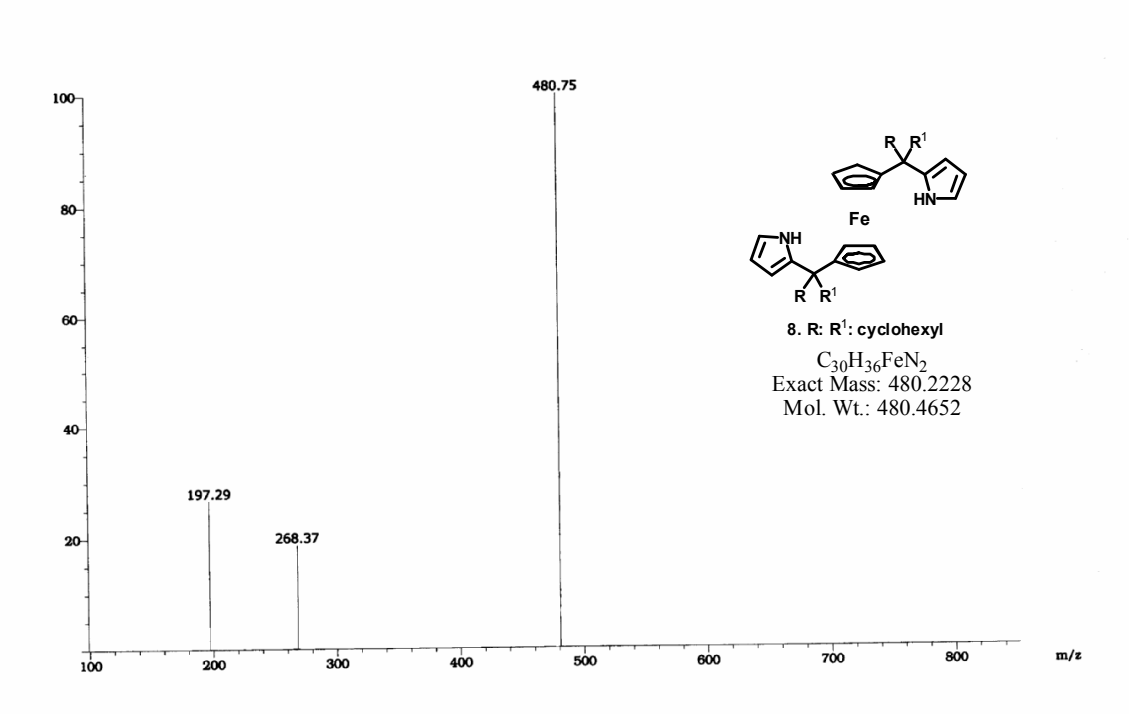


Figure – 1: Mass Spectrum of **9**

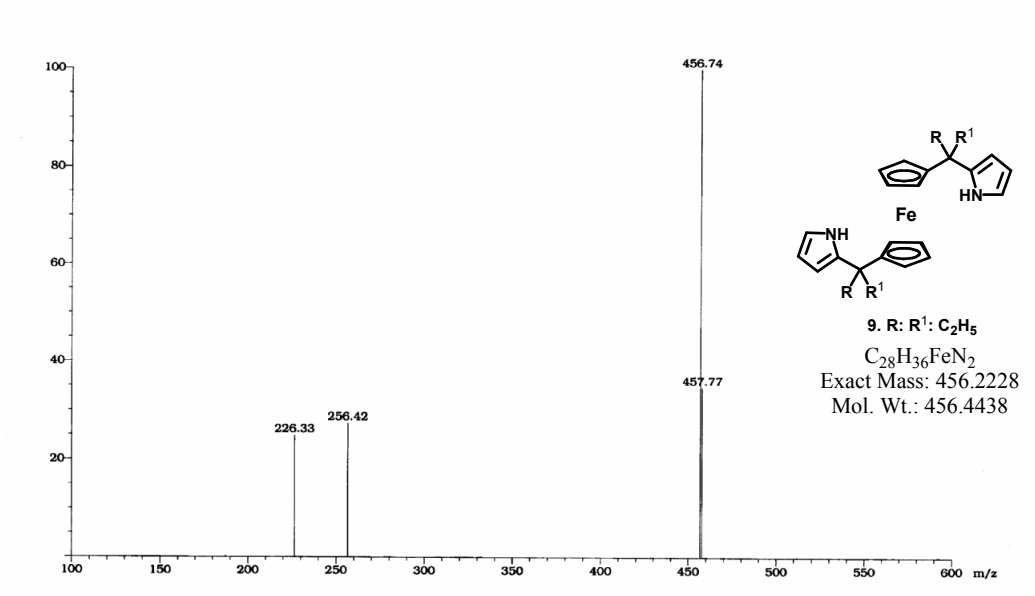


Figure – 1: Mass Spectrum of **10**

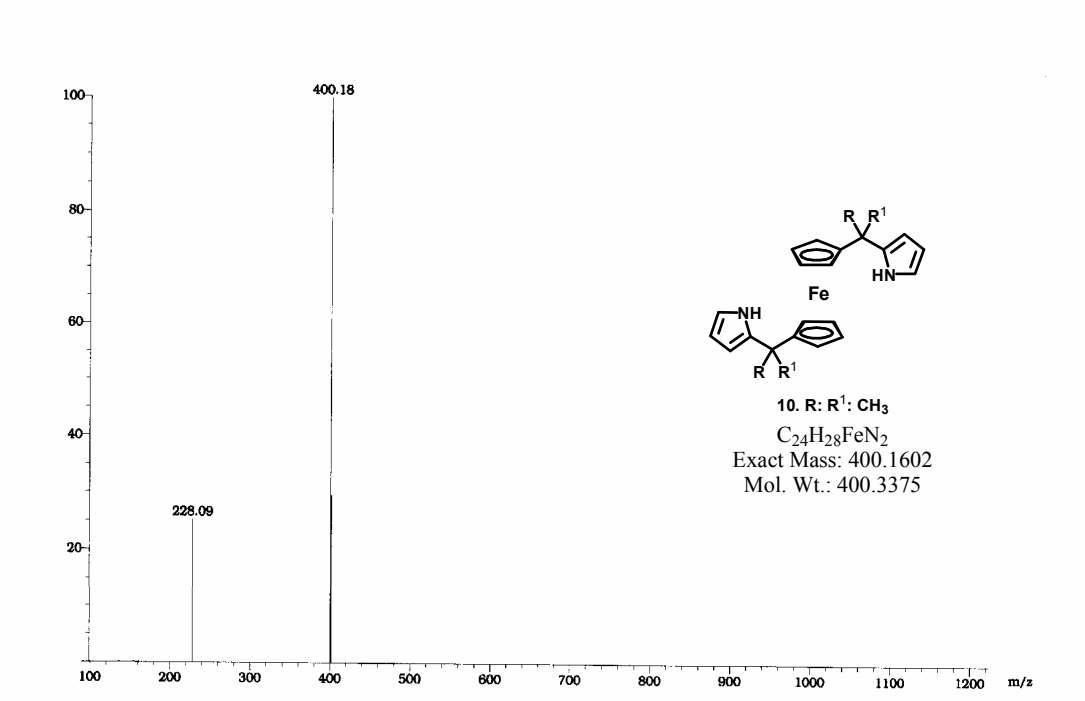


Figure – 2: Mass Spectrum of **11**

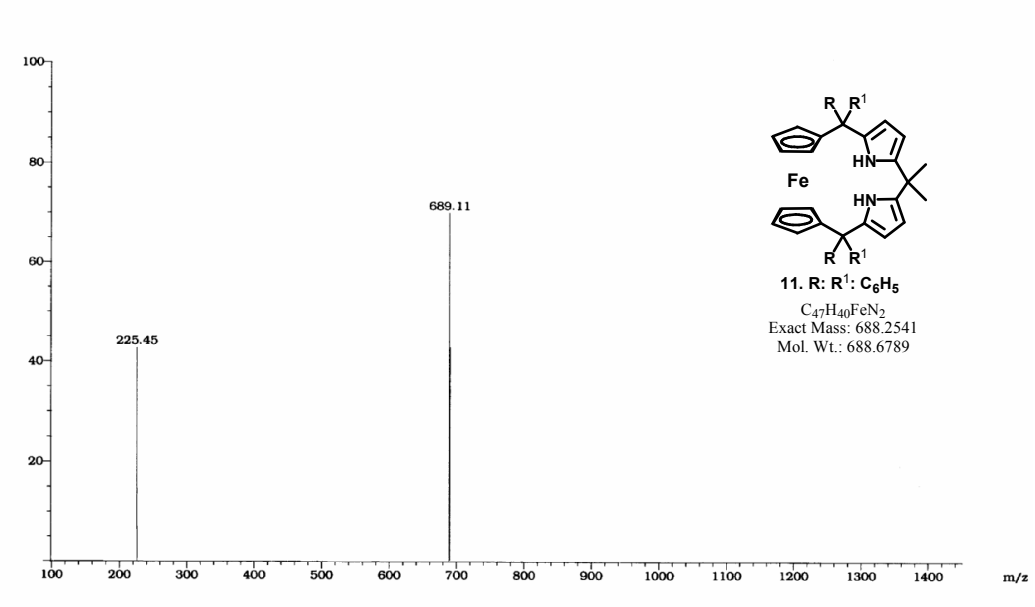


Figure – 2: Mass Spectrum of **12**

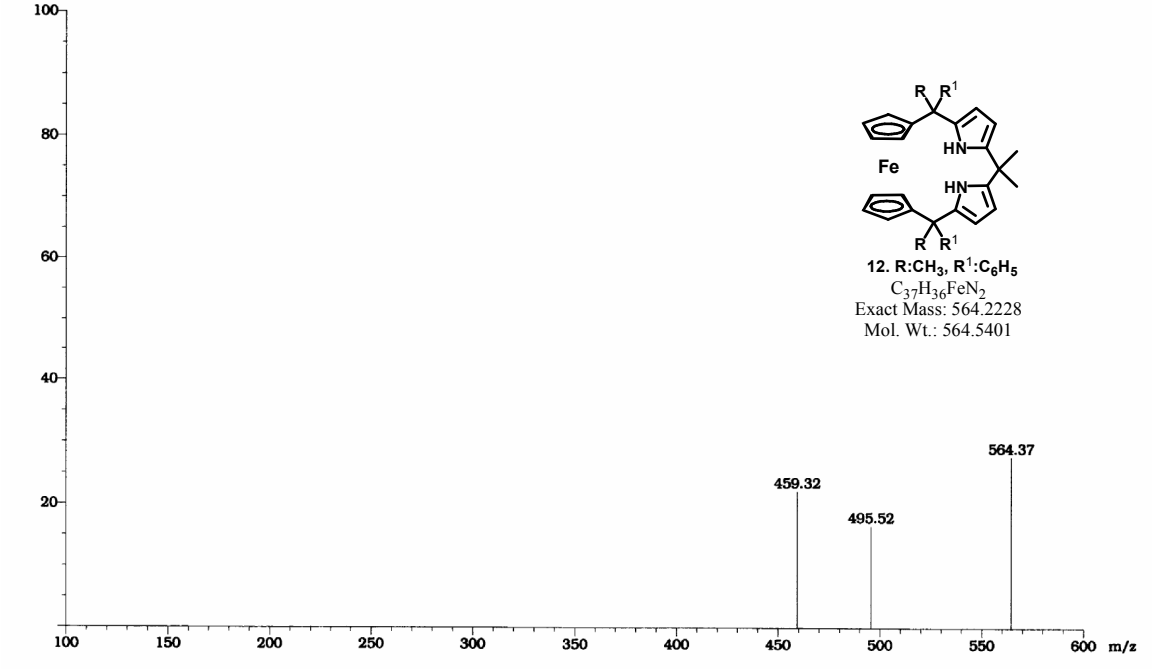


Figure – 2: Mass Spectrum of **13**

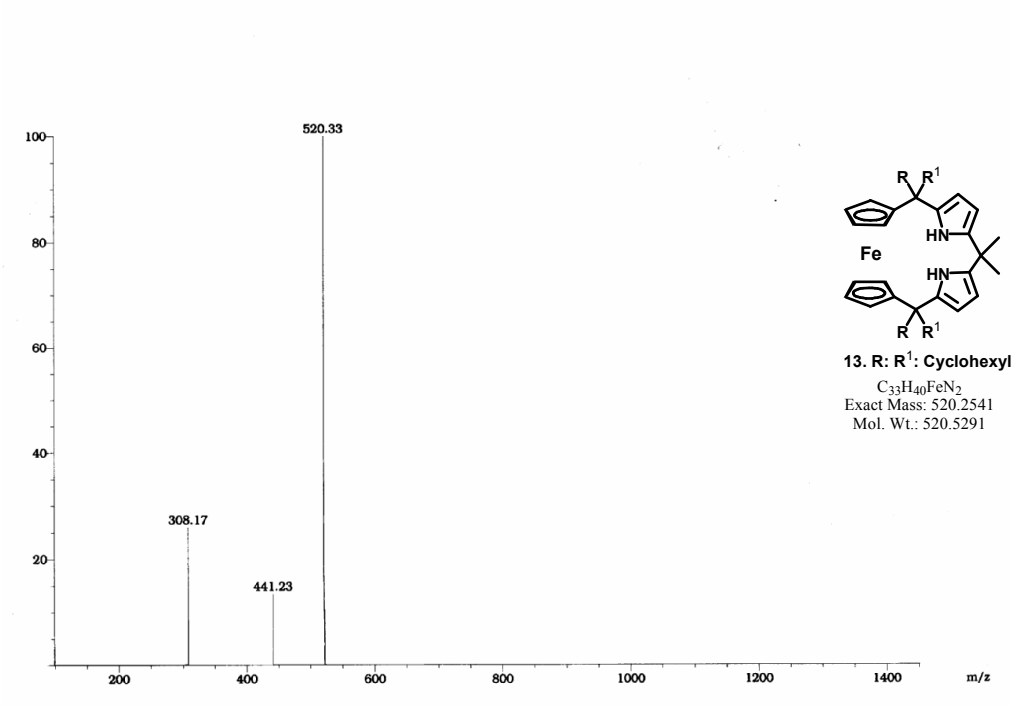


Figure – 2: Mass Spectrum of **14**

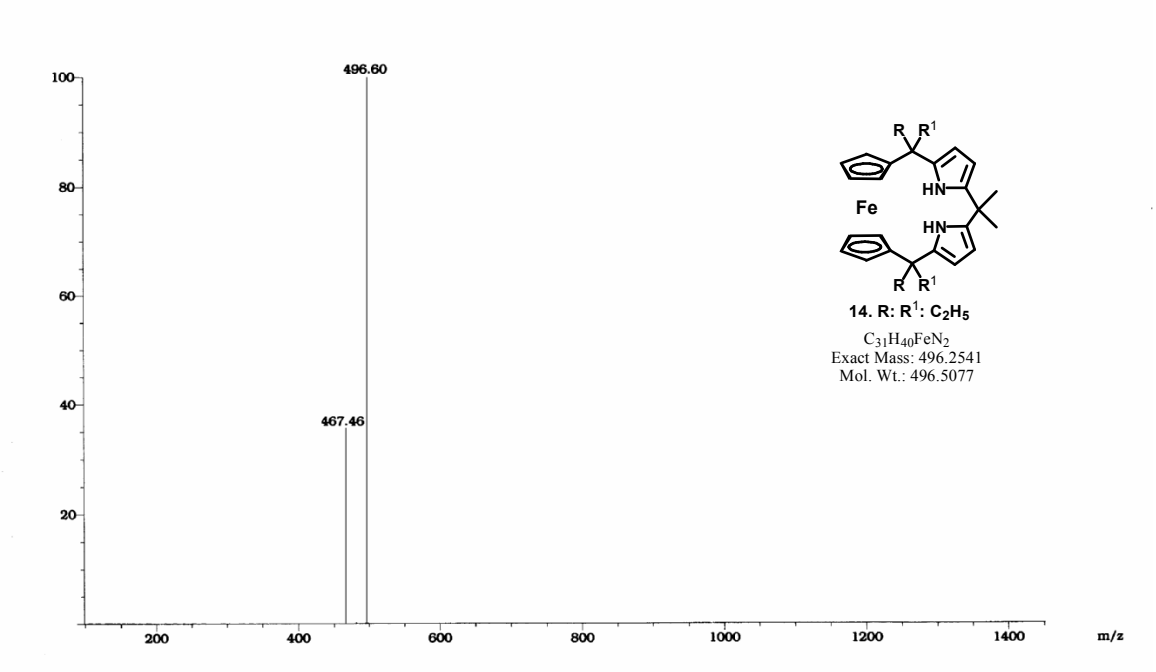


Figure – 2: Mass Spectrum of **15**

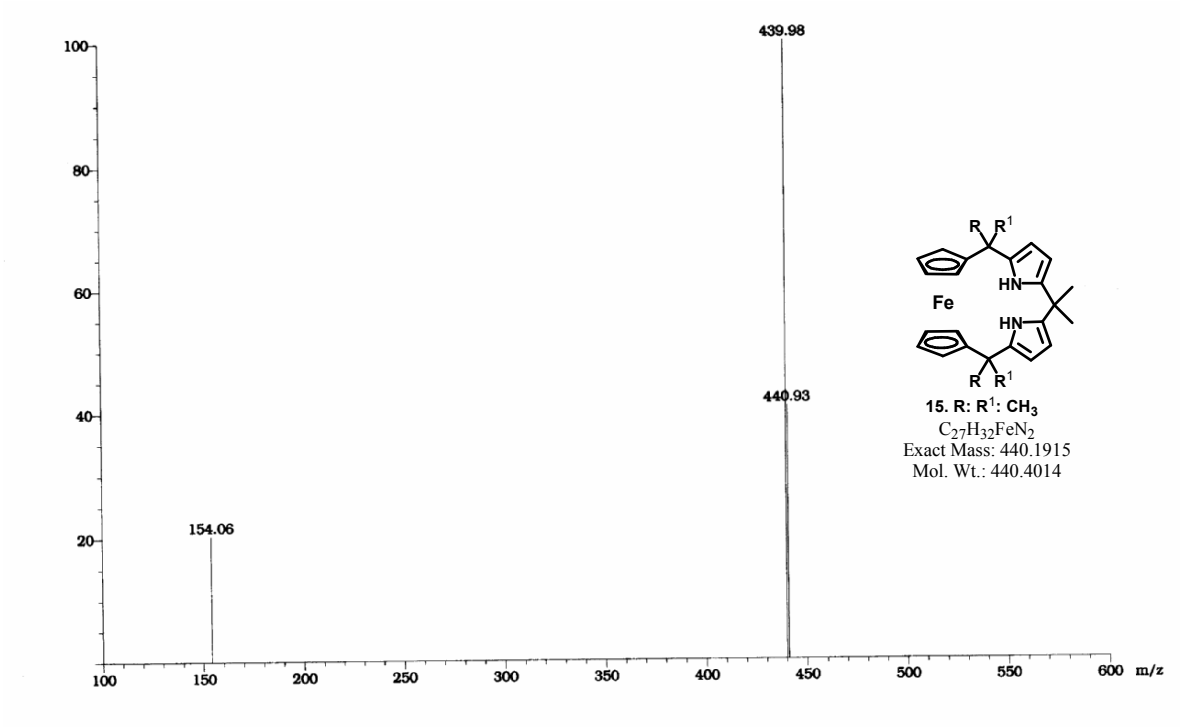


Figure – 2: Mass Spectrum of **16**

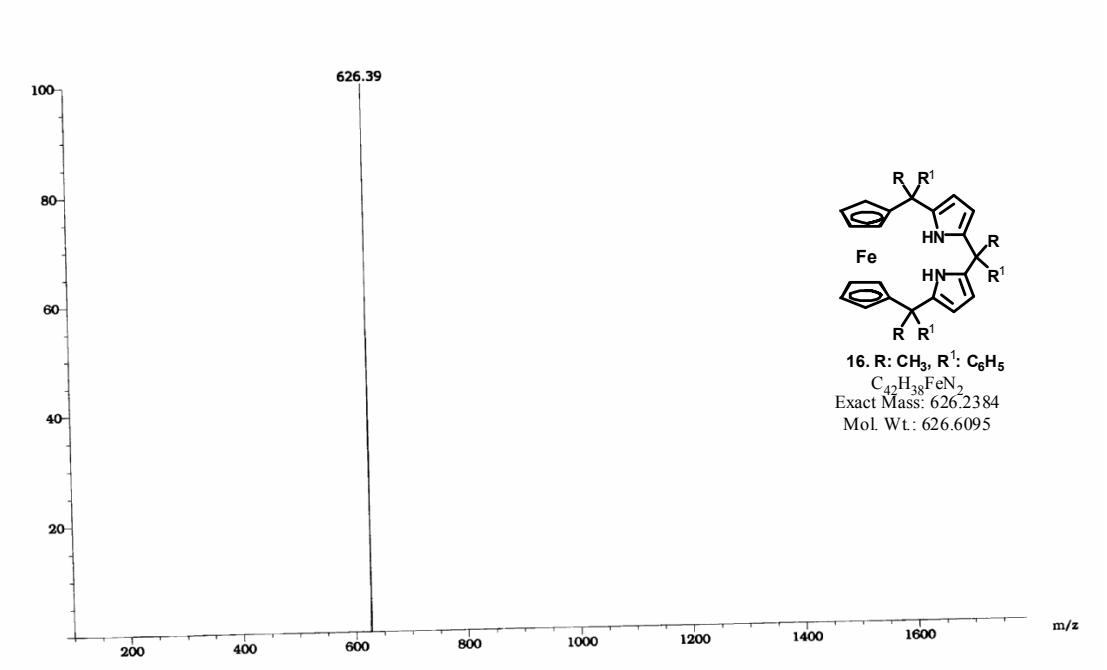


Figure – 2: Mass Spectrum of **17**

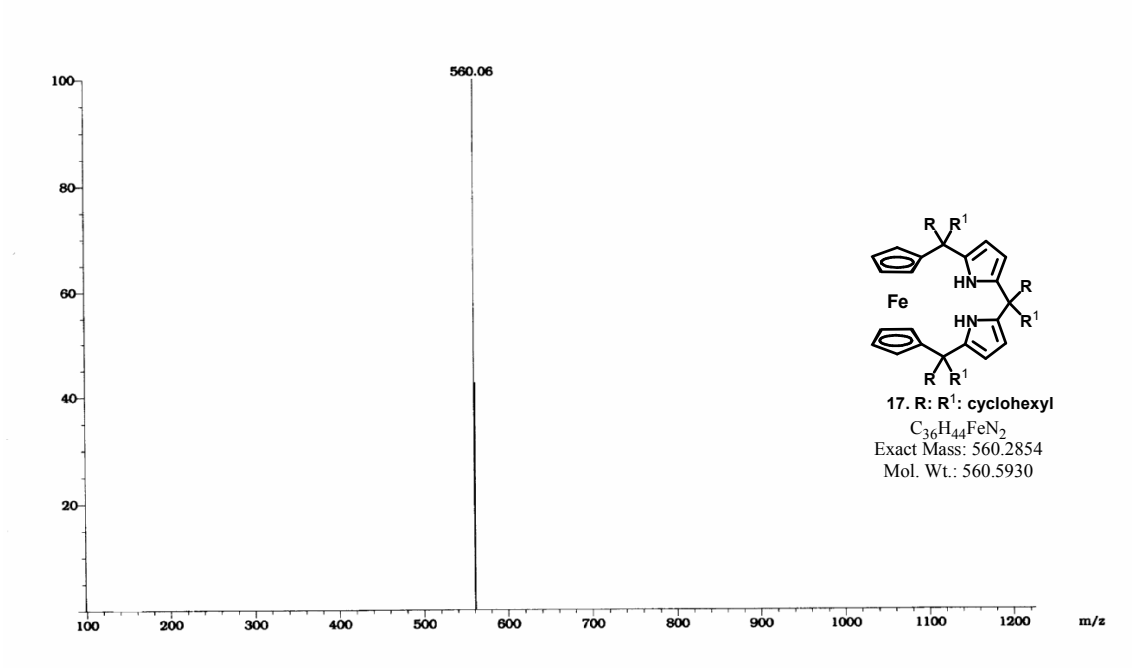


Figure – 2: Mass Spectrum of **18**

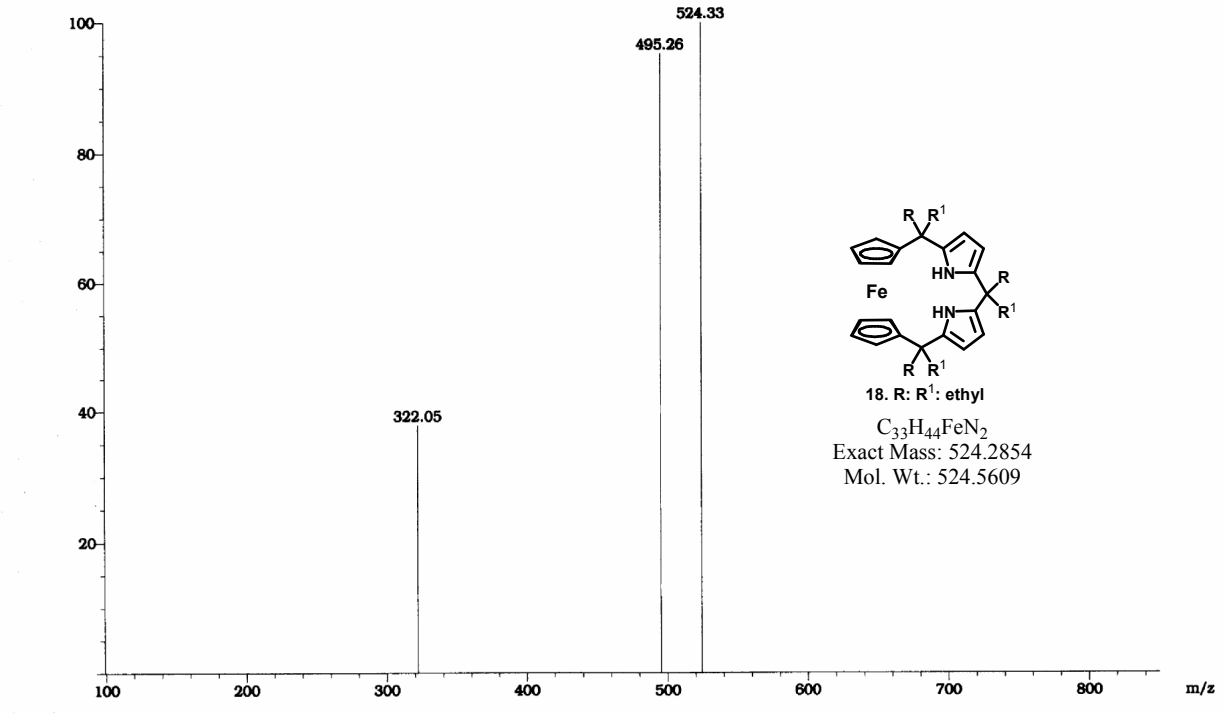


Figure – 1: Mass Spectrum of **24**

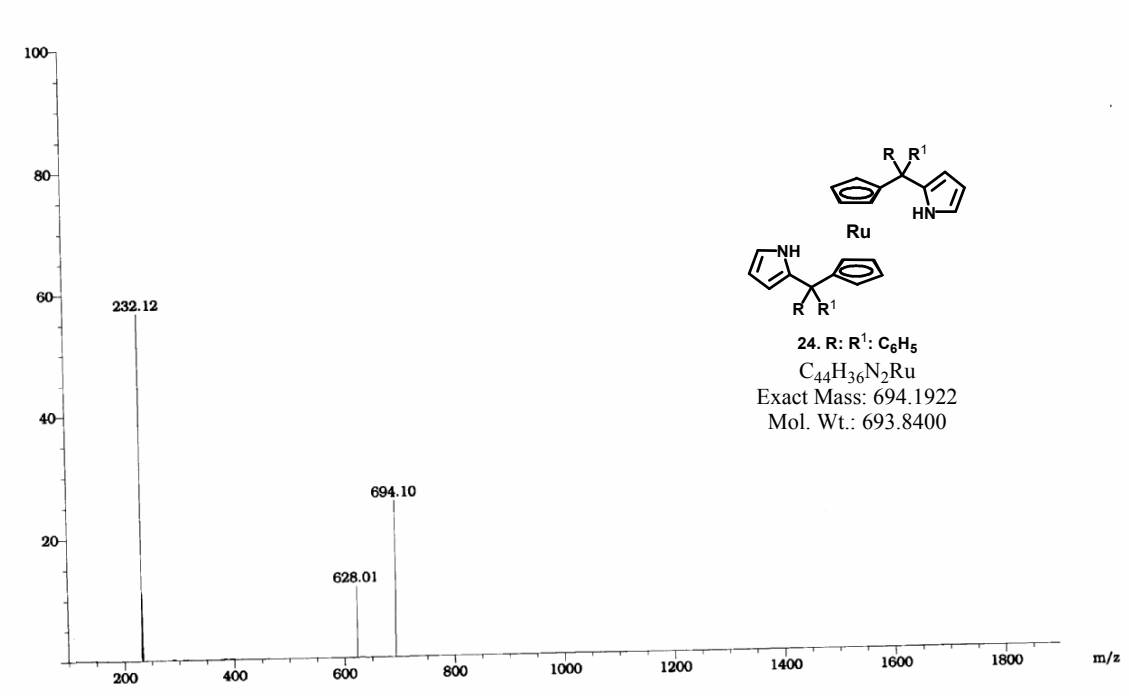


Figure – 2: Mass Spectrum of **25**

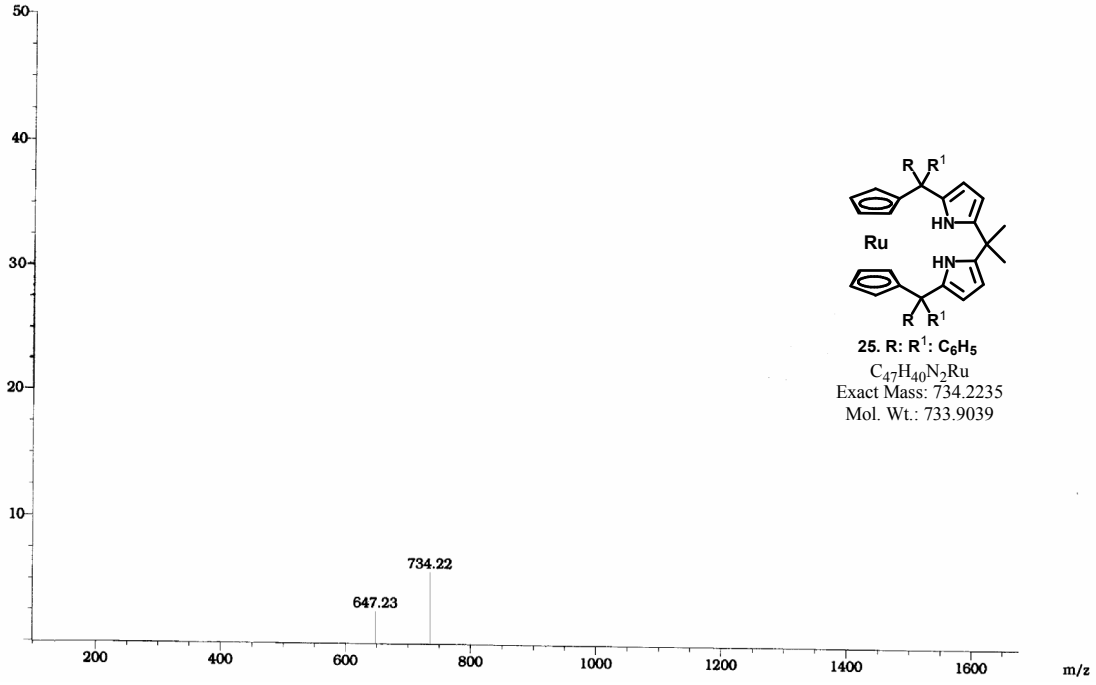


Figure – 3: Mass Spectrum of Expanded derivative of **15** (2 : 2 product):

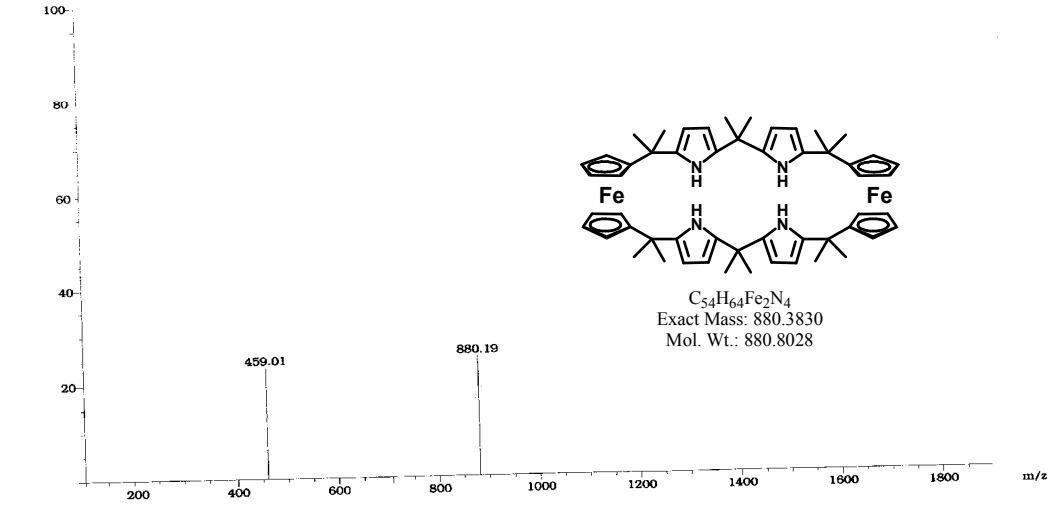


Figure – 3: Mass Spectrum of Expanded derivative of **15** (3 : 3 product):

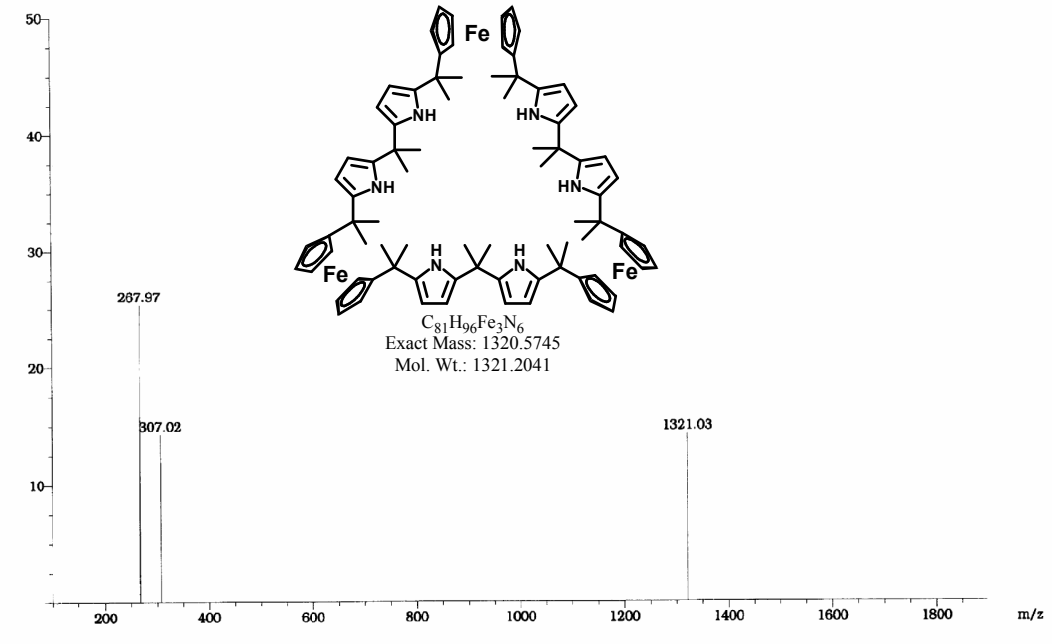


Figure – 4: ^{1}H NMR spectrum of **6**

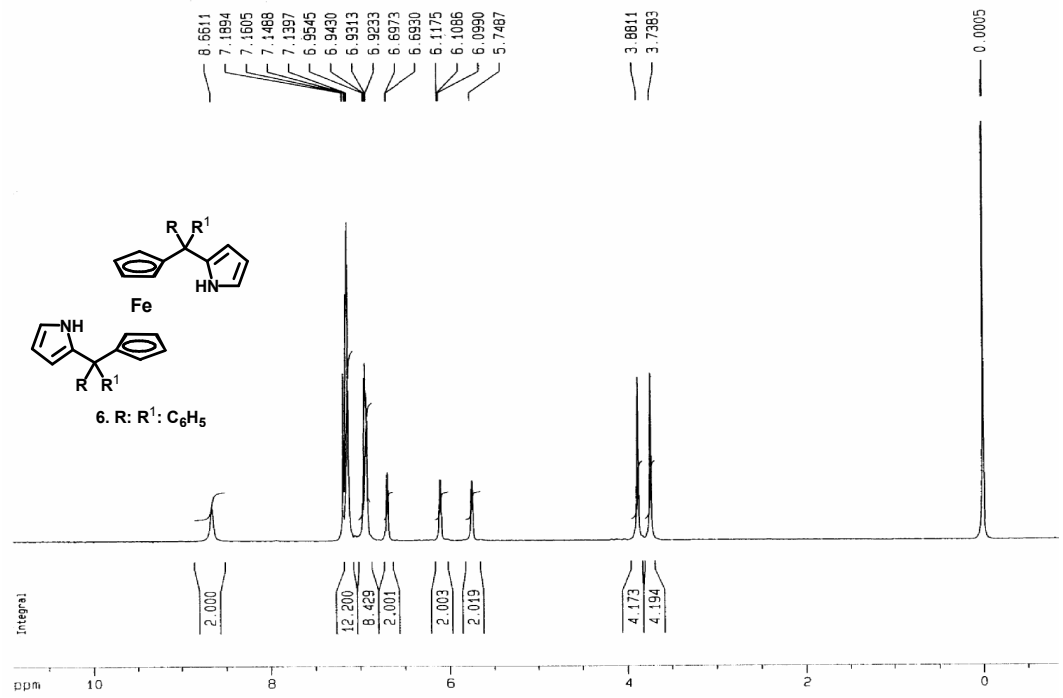


Figure – 4: ^{1}H NMR spectrum of **7**

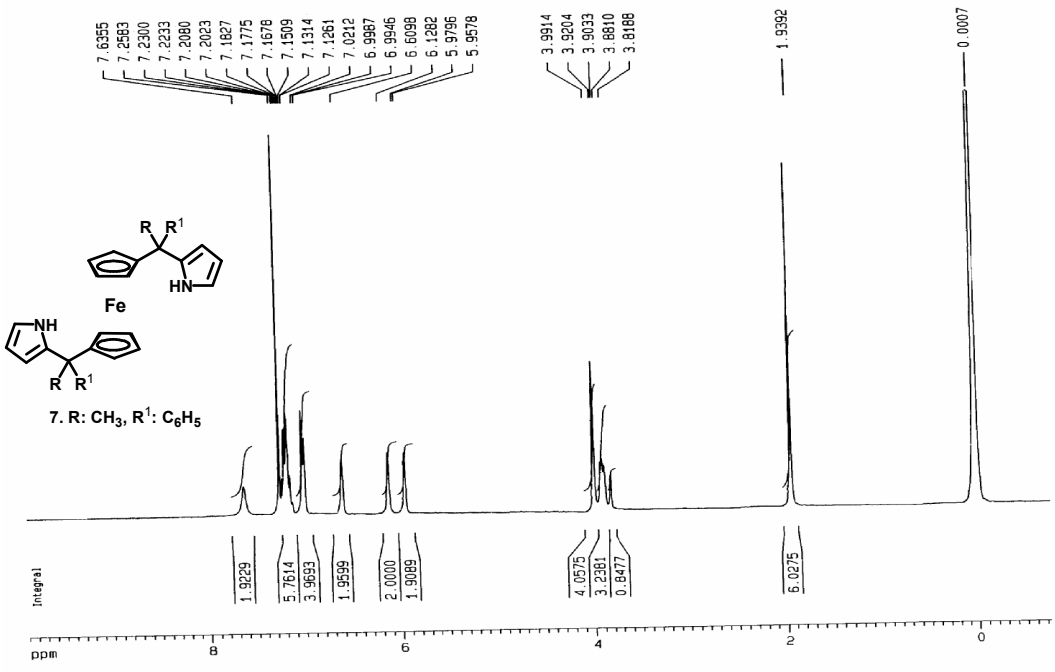


Figure – 4: ^{1}H NMR spectrum of **8**

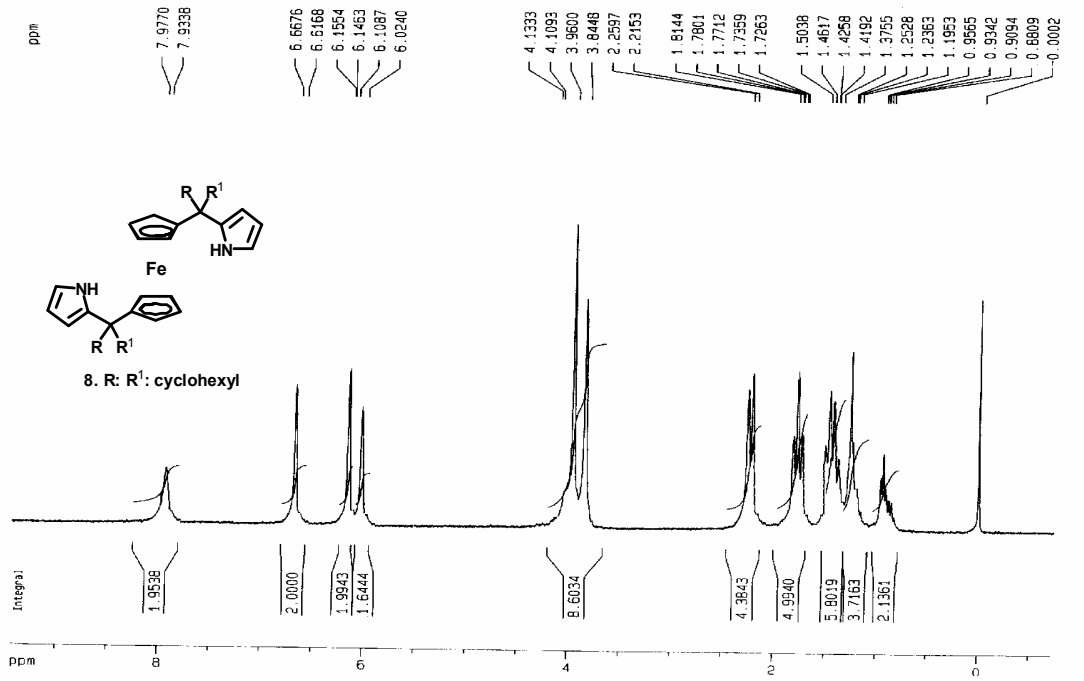


Figure – 4: ^{1}H NMR spectrum of **9**

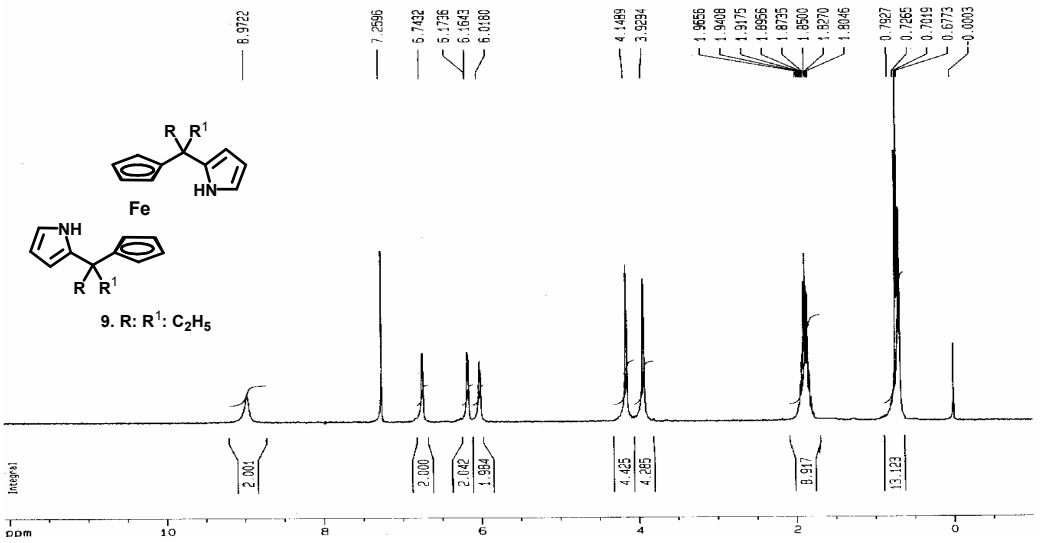


Figure – 4: ^{1}H NMR spectrum of **10**

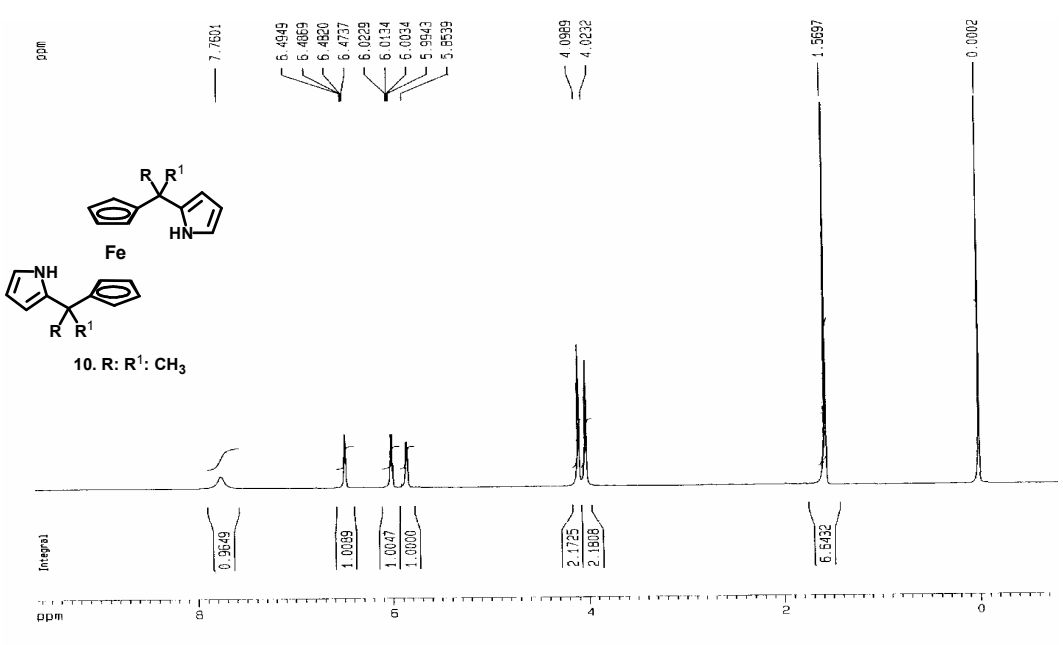


Figure – 5: ^{1}H NMR spectrum of **12**

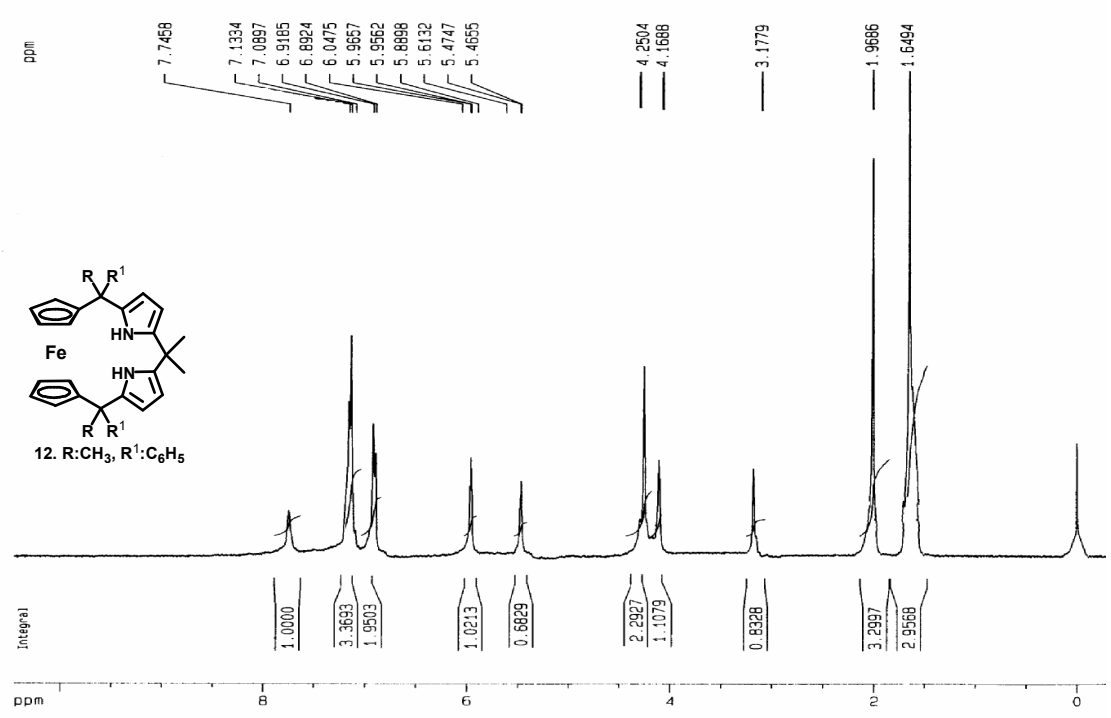


Figure – 5: ^{1}H NMR spectrum of **13**

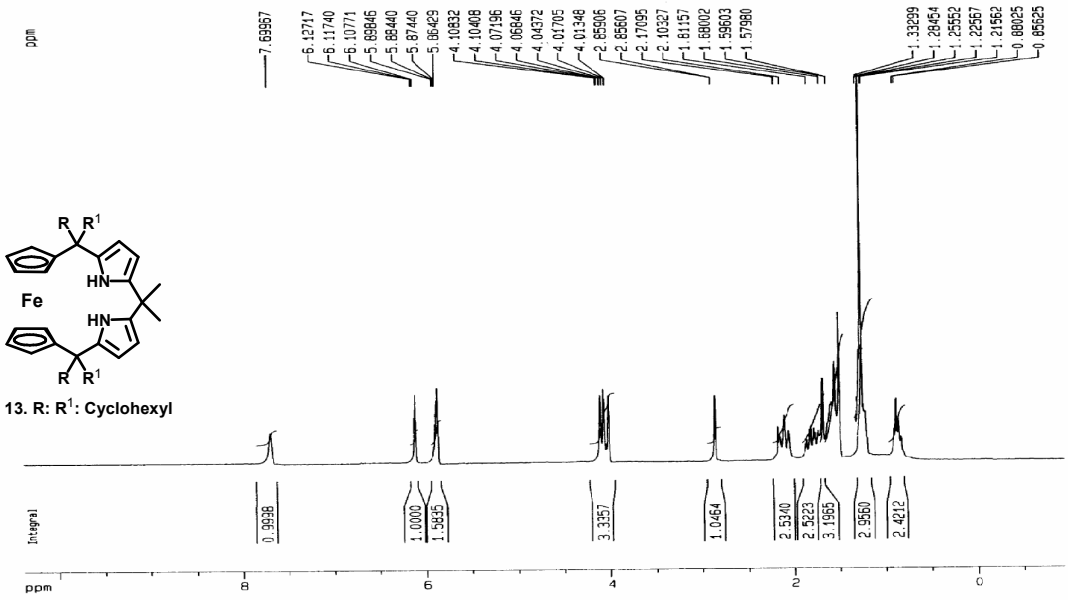


Figure – 5: ^{1}H NMR spectrum of **14**

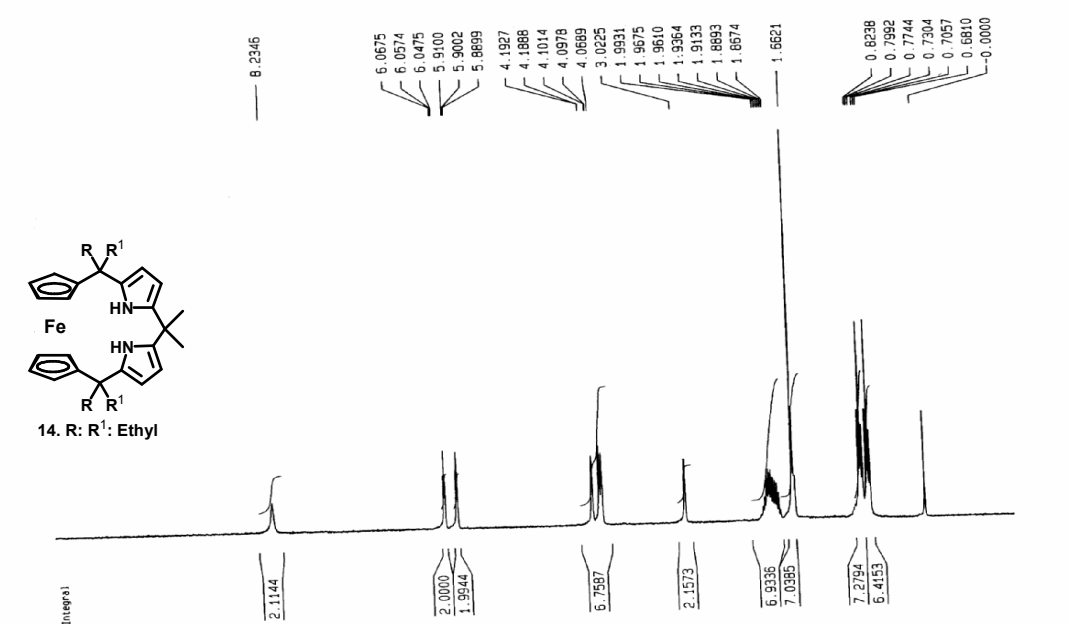


Figure – 5: ^{1}H NMR spectrum of **16**

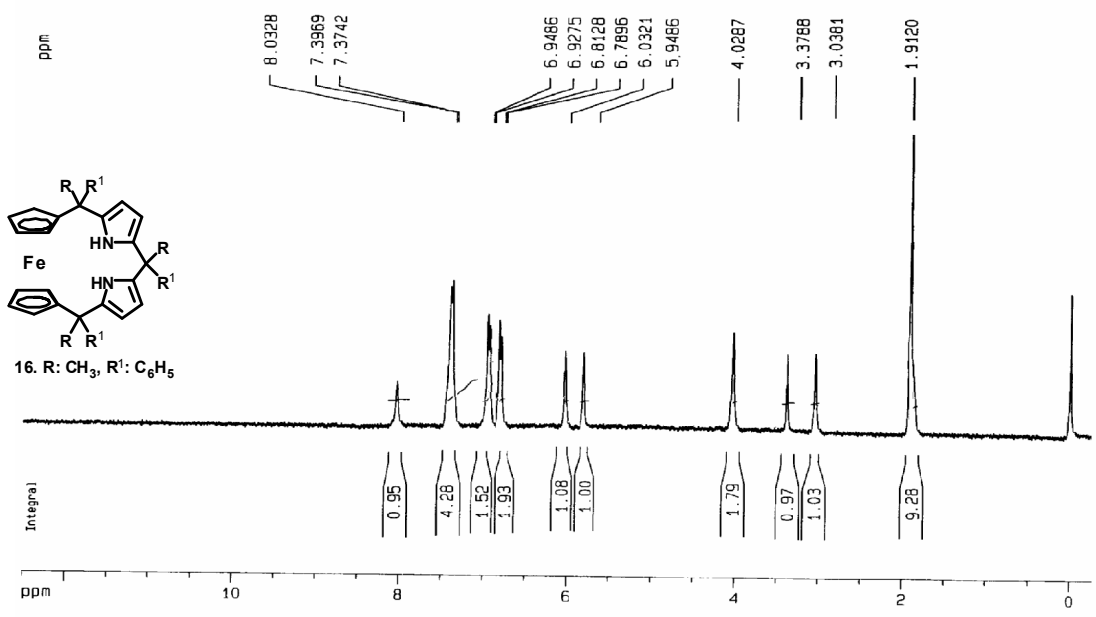


Figure – 5: ^{1}H NMR spectrum of **17**

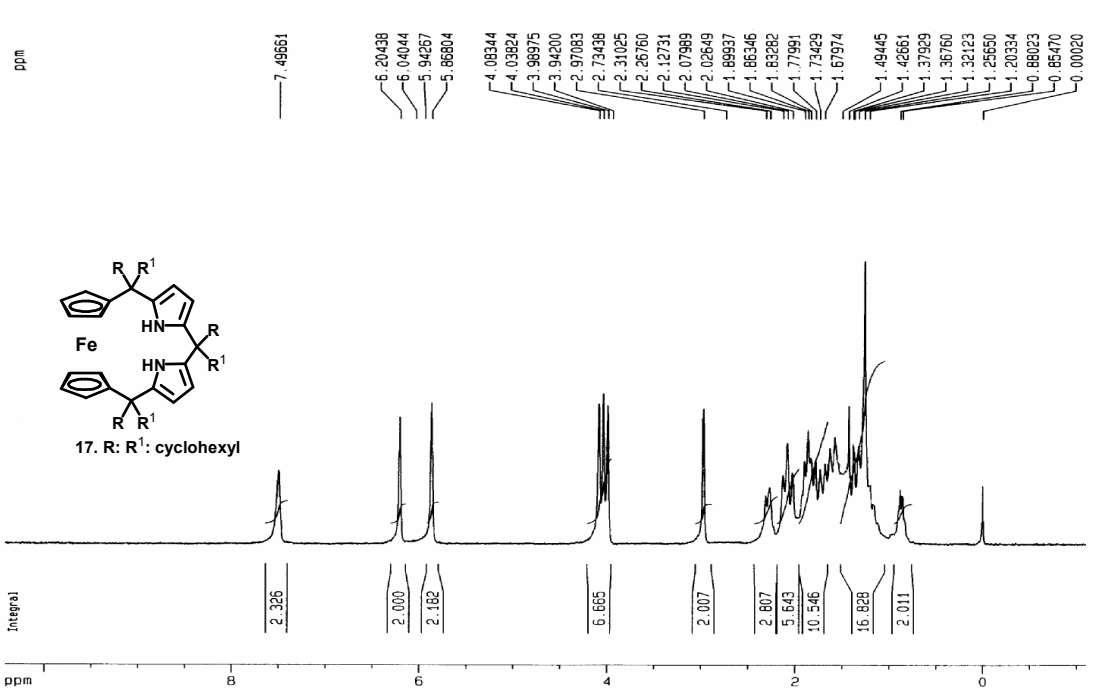


Figure – 5: ^{1}H NMR spectrum of **18**

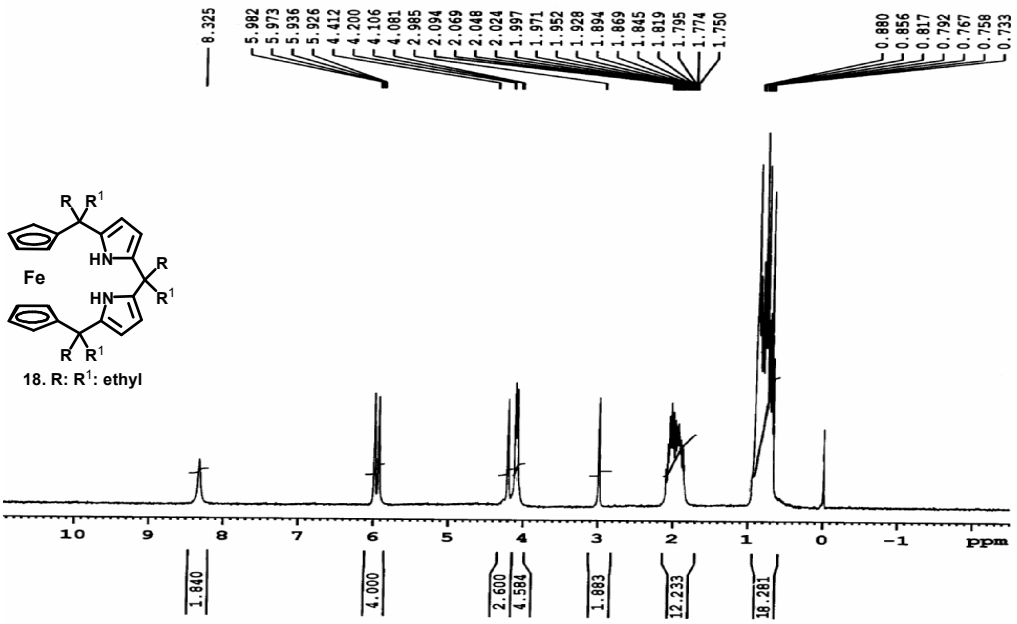


Figure – 4: ^{1}H NMR spectrum of **24**

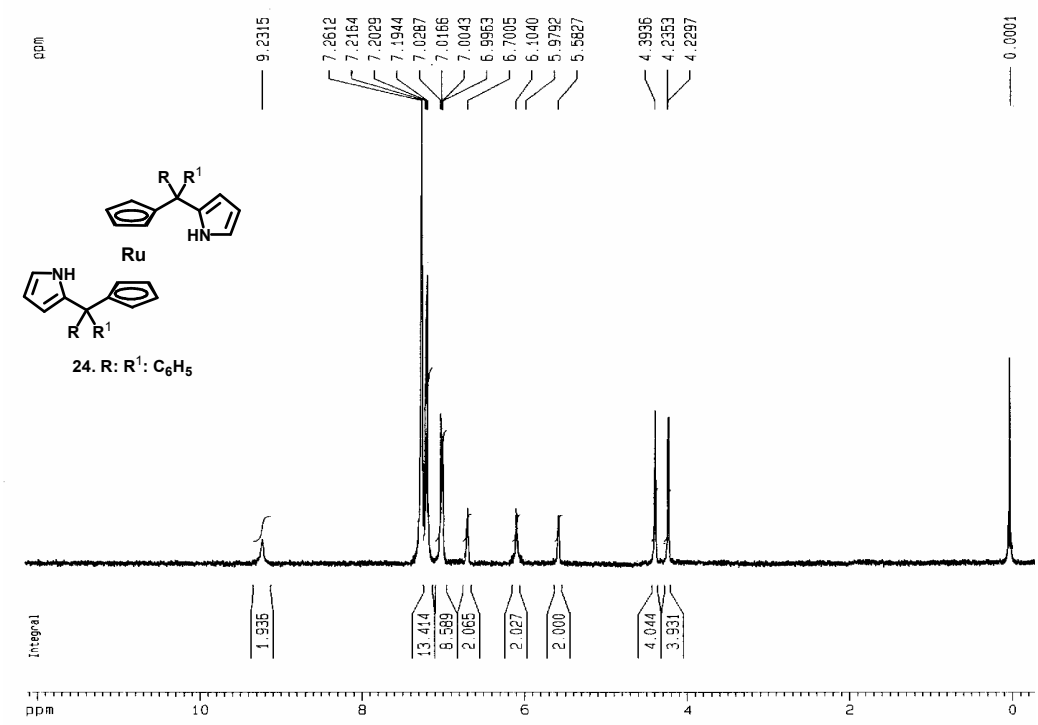


Figure – 5: ^{1}H NMR spectrum of **25**

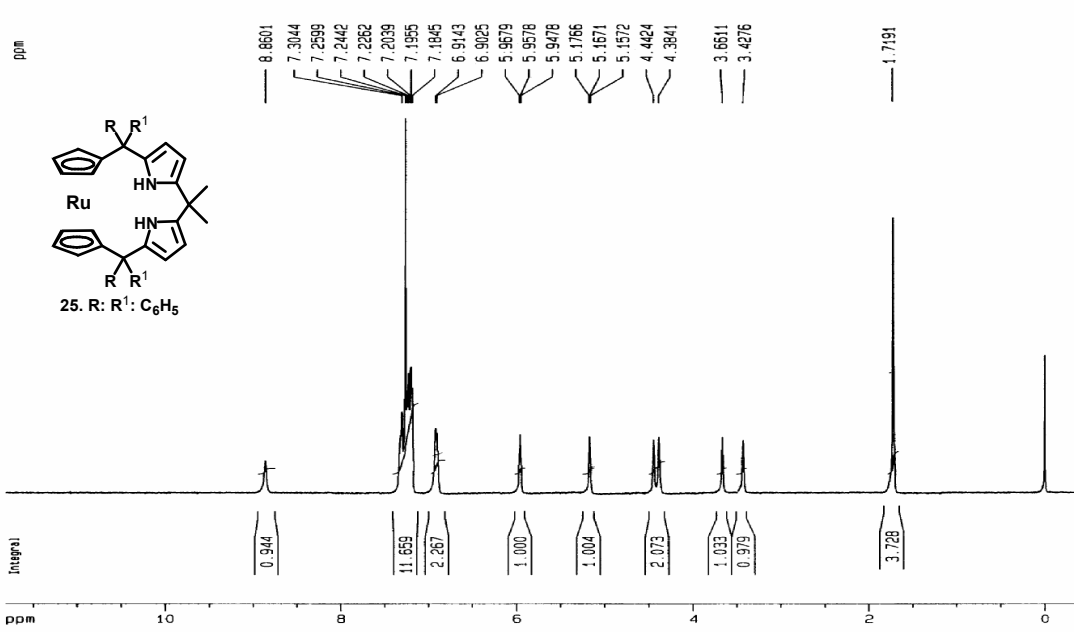


Figure – 6: ^{13}C Spectrum of **6**

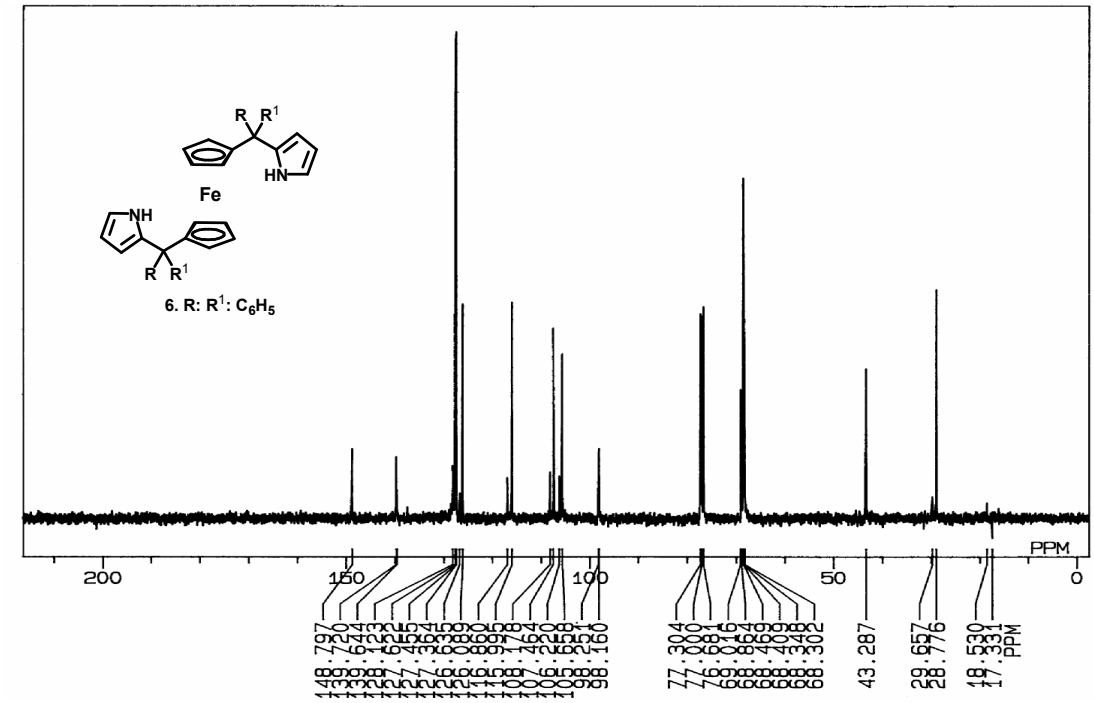


Figure – 6: ^{13}C Spectrum of **7**

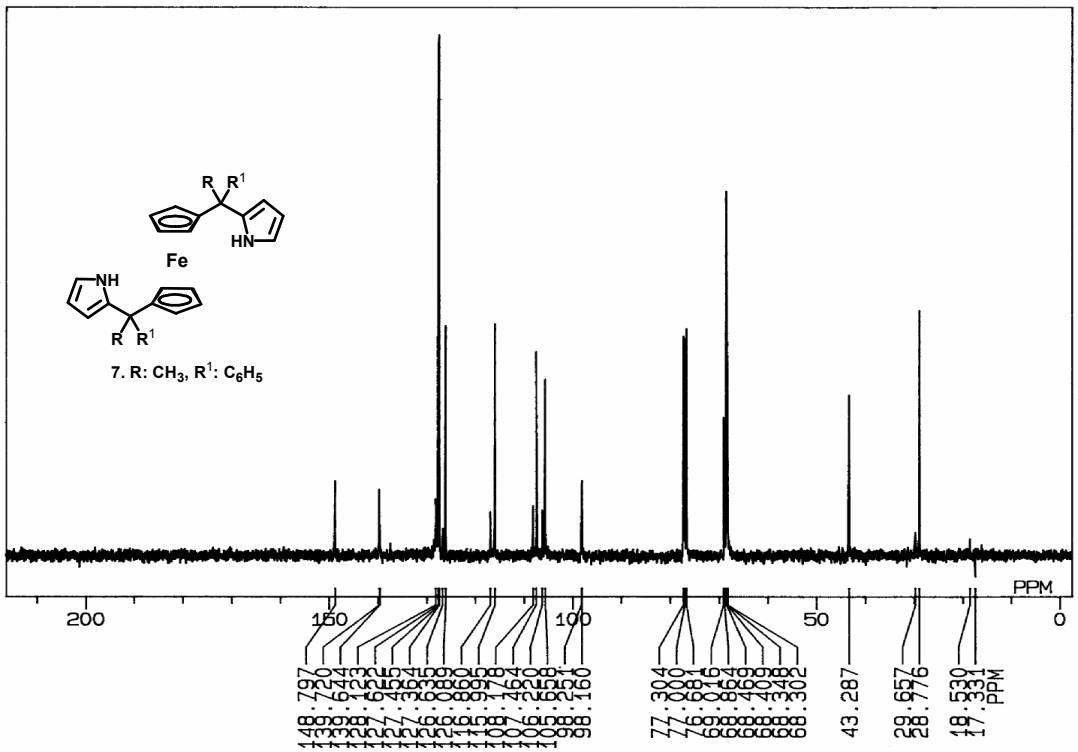


Figure – 6: ^{13}C Spectrum of **9**

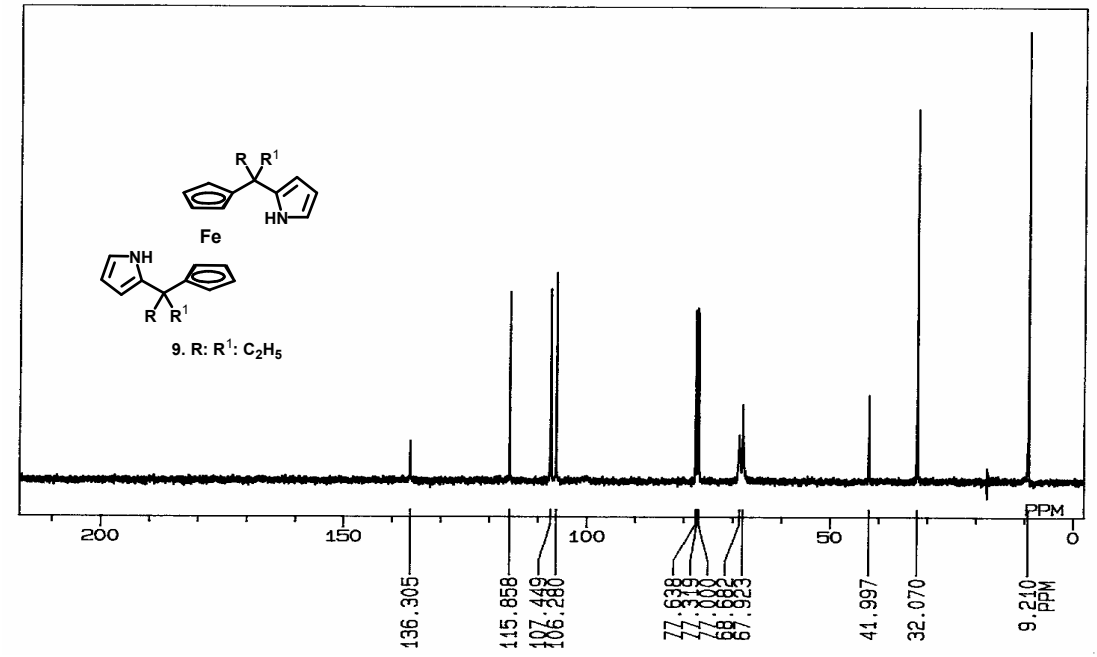


Figure – 6: ^{13}C Spectrum of **10**

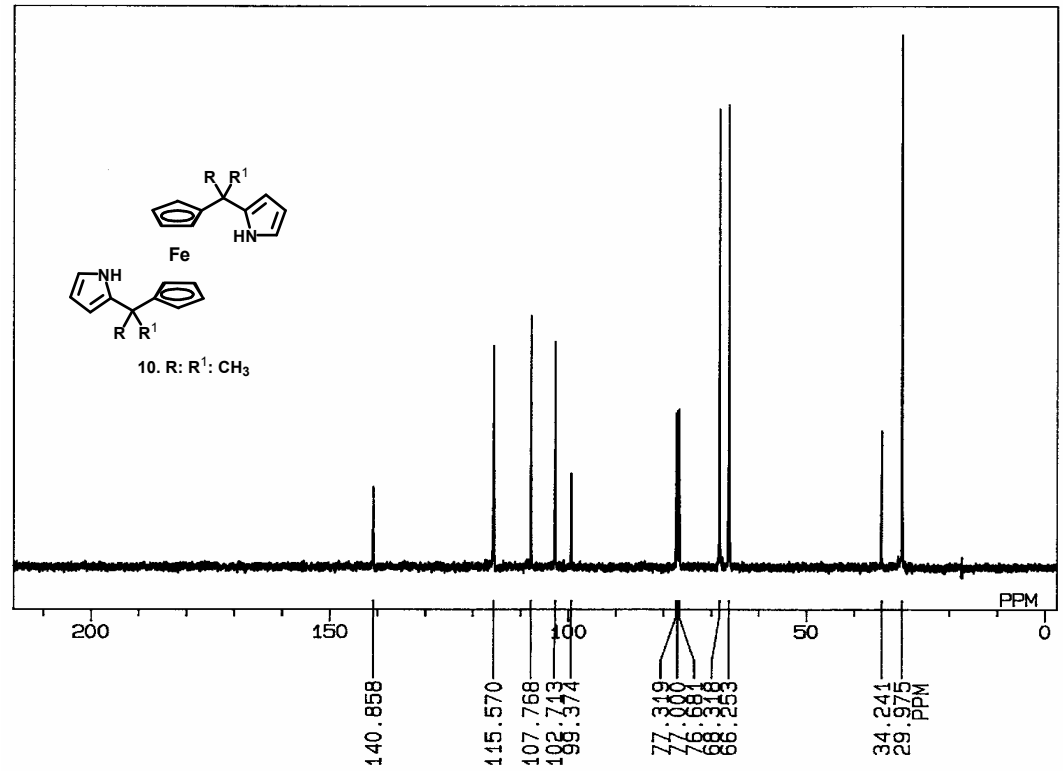


Figure – 7: ^{13}C Spectrum of **14**

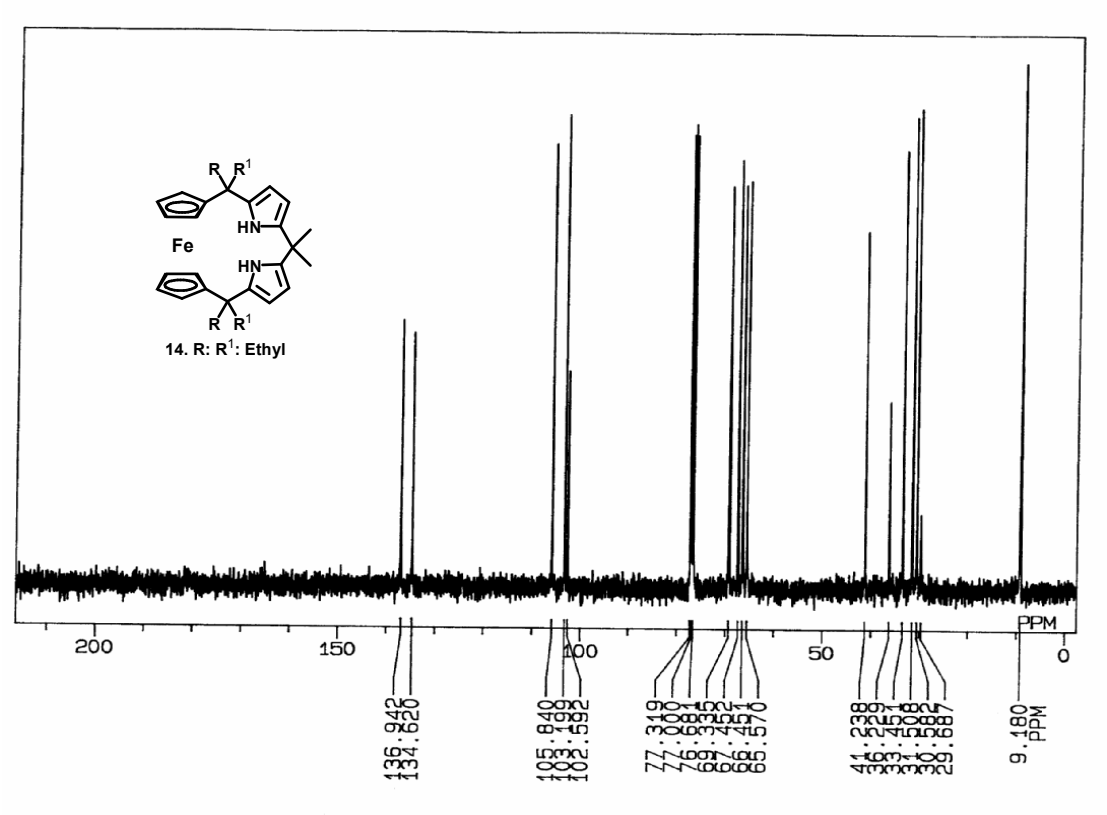


Figure – 7: ^{13}C Spectrum of **17**

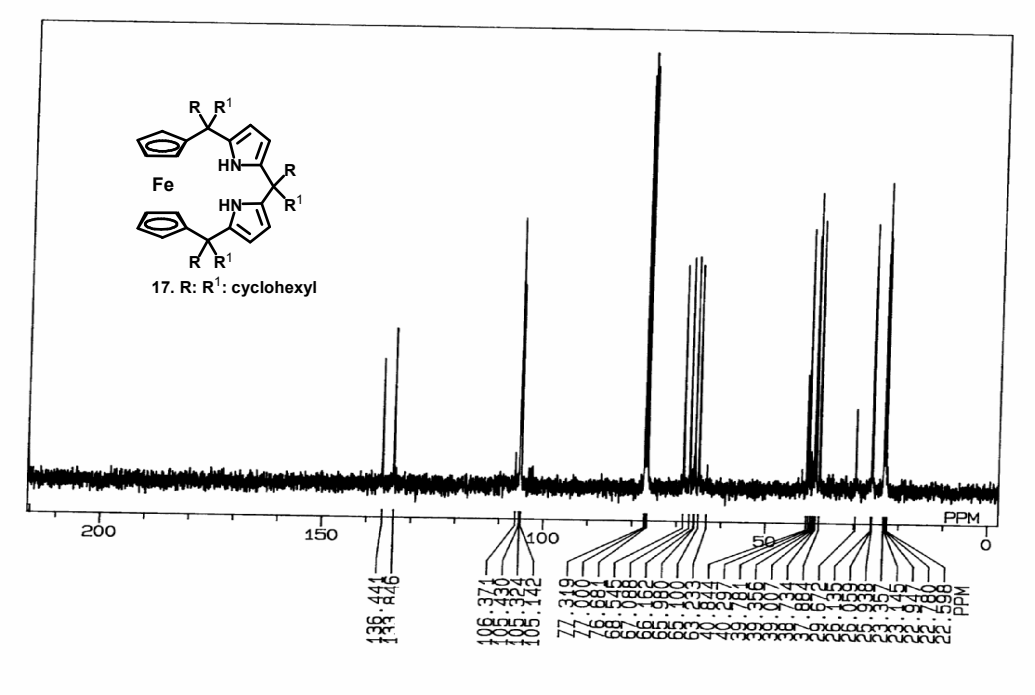
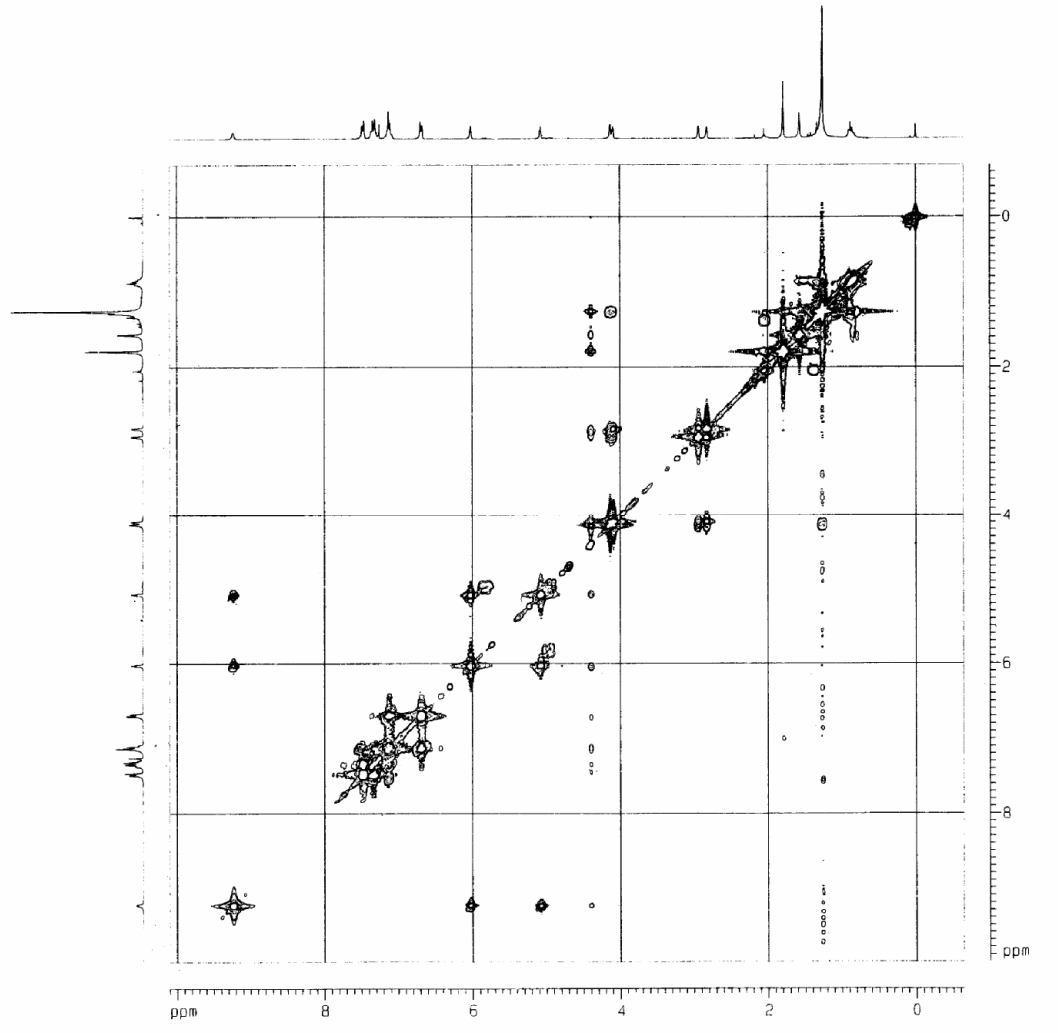
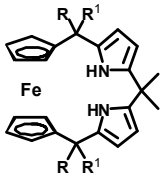


Figure – 8: $^{1}H - {}^{1}H$ COSY spectrum of **11**





11. R: R^1: C_6H_5

Figure – 8: ^{1}H – ^{1}H COSY spectrum of **11** shows the correlation between pyrrolic NH

and β-CH protons

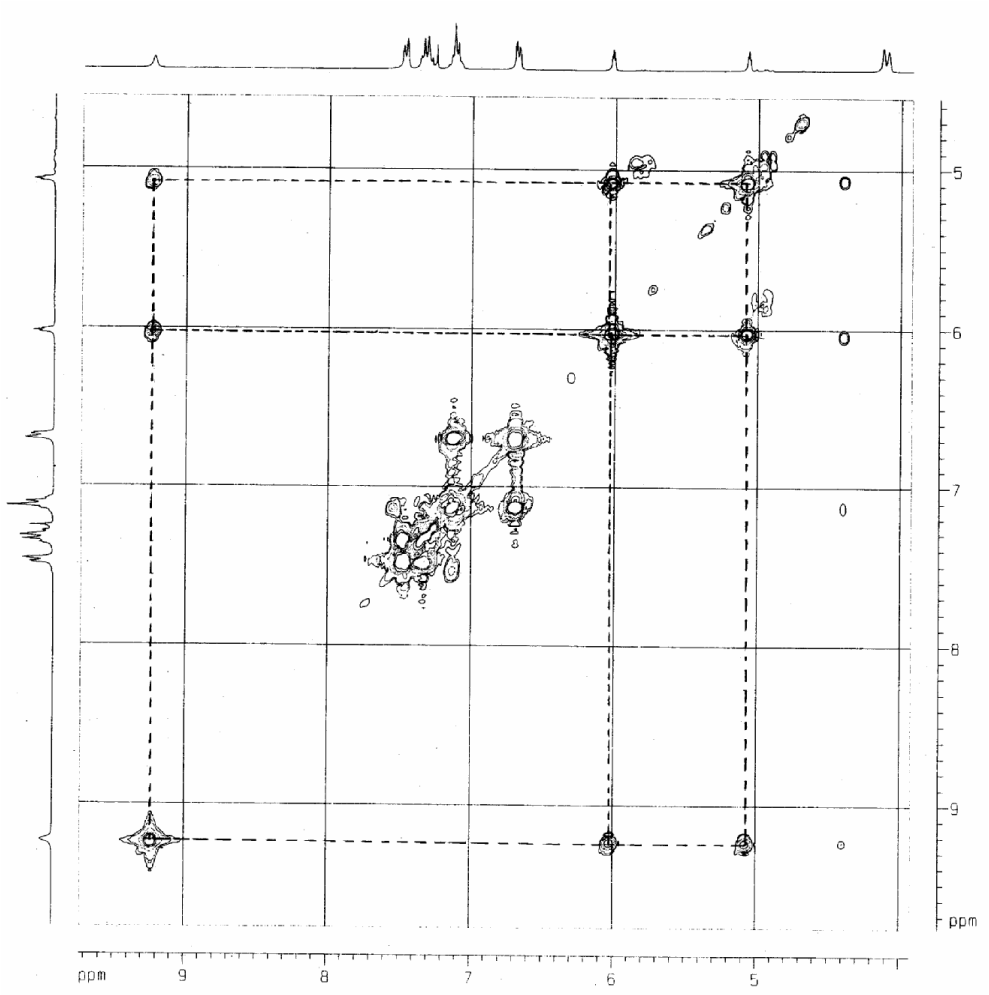
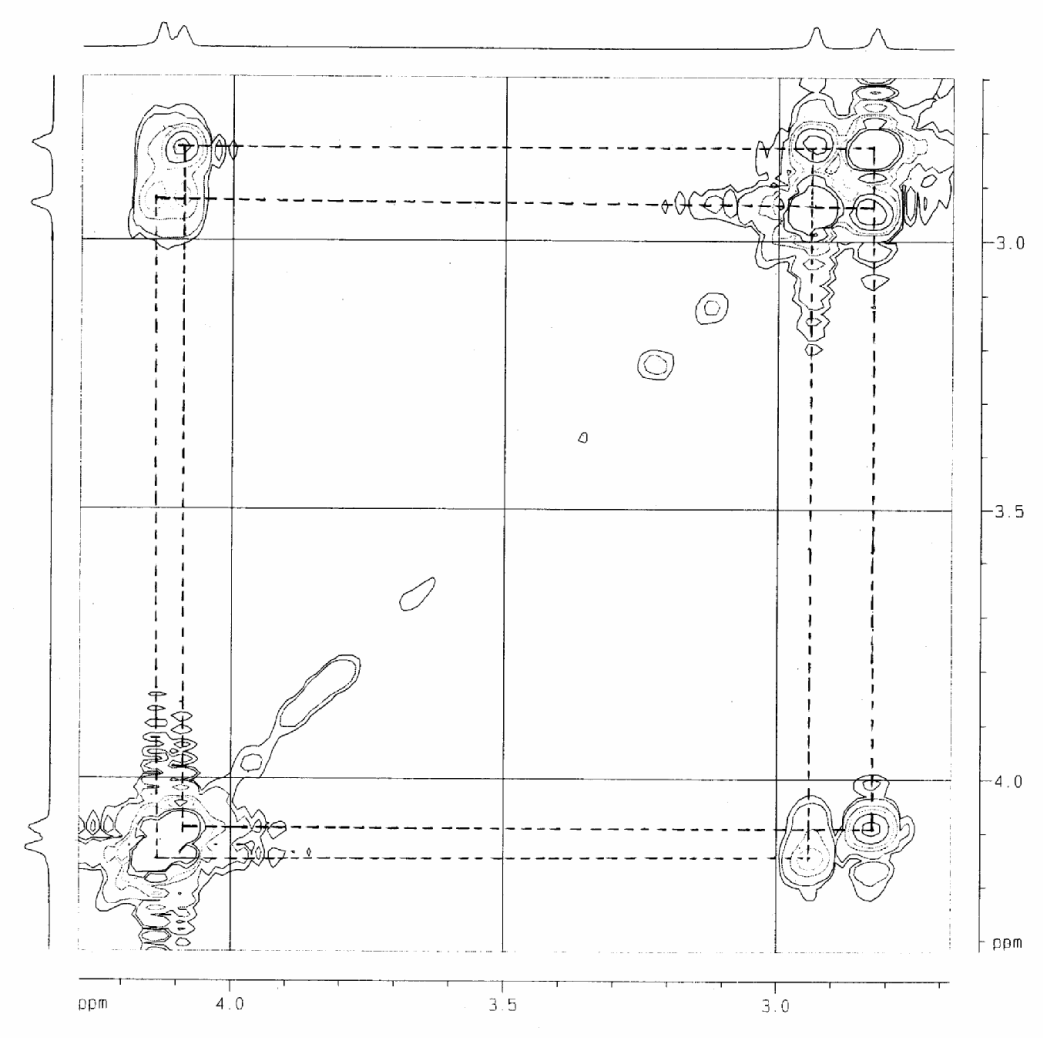
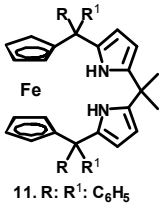


Figure – 8: $^{1}H - {}^{1}H$ COSY spectrum of **11** shows correlation in the Ferrocenyl-CH

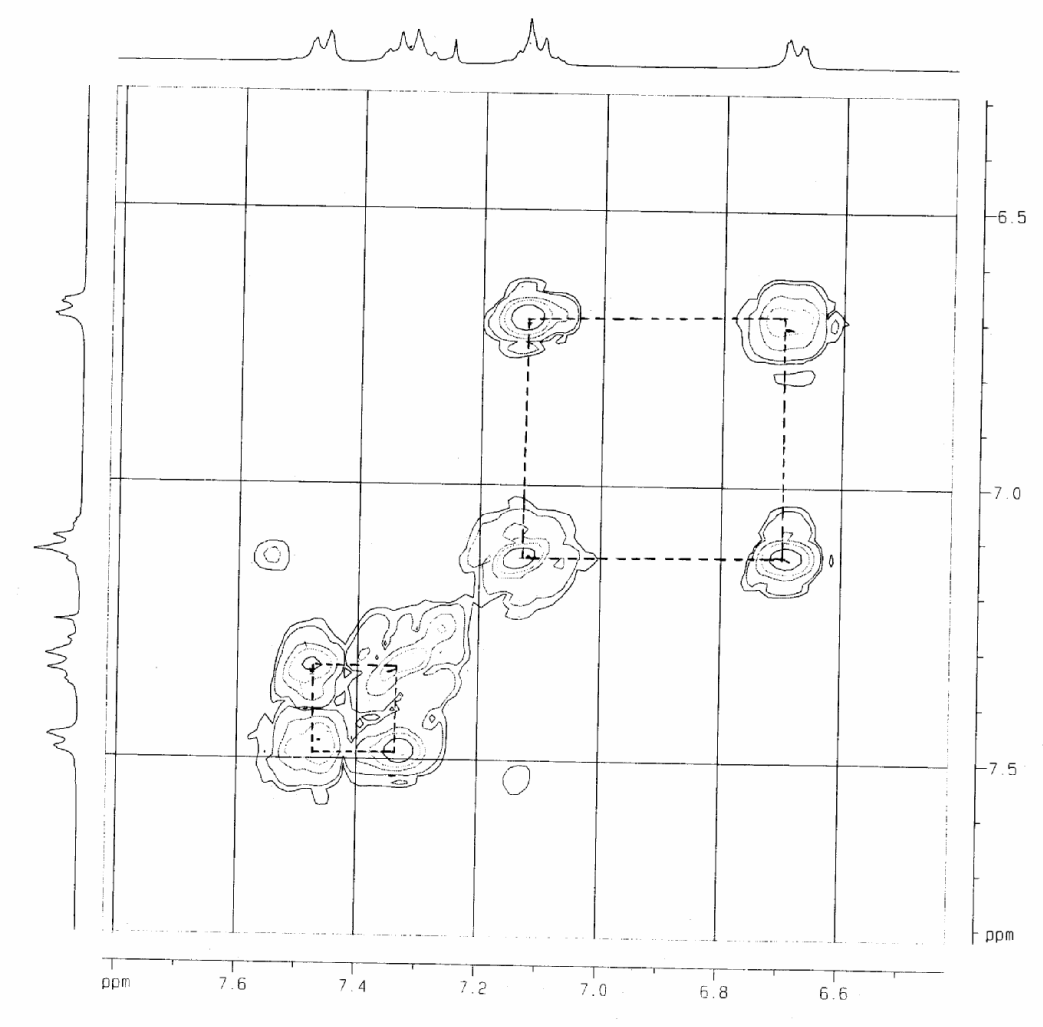
protons

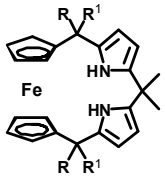




11. R: R^1: C_6H_5

Figure – 8: ^{1}H – ^{1}H COSY spectrum of **11** shows correlation in the phenyl-CH protons





11. R: R^1: C_6H_5

Table – 1: The shift difference observed in the pyrrolic β-CH and Ferrocenyl CH protons of macrocycle and dipyrromethane.

No.	Pyrrolic β-CH*	Ferrocenyl – CH
11 – 6	5.55 – 5.93: (–0.38)	3.28 – 3.81: (–0.53)
12 – 7	5.71– 6.05: (–0.34)	3.86 – 3.91: (–0.05)
13 – 8	6.00 – 6.09: (–0.09)	3.46 – 3.9: (–0.44)
14 – 9	5.98 – 6.10: (–0.12)	3.77 – 4.04: (–0.27)
15 – 10	5.92 – 5.93: (–0.01)	3.65 – 4.06: (–0.41)
16 – 7	5.99 – 6.05: (–0.06)	3.48 – 3.91: (–0.43)
17 – 8	6.04 – 6.09: (–0.05)	3.77 – 3.90: (–0.13)
18 – 9	5.95 – 6.10: (–0.15)	3.76 – 4.04: (–0.28)
25 – 24	5.57 – 5.84: (–0.27)	3.98 – 4.32: (–0.34)

*For calculation, pyrrolic α -CH protons of **6** – **10** and **24** are not included.

Figure – 9: Single crystal X-ray Structure of **6** (top view):

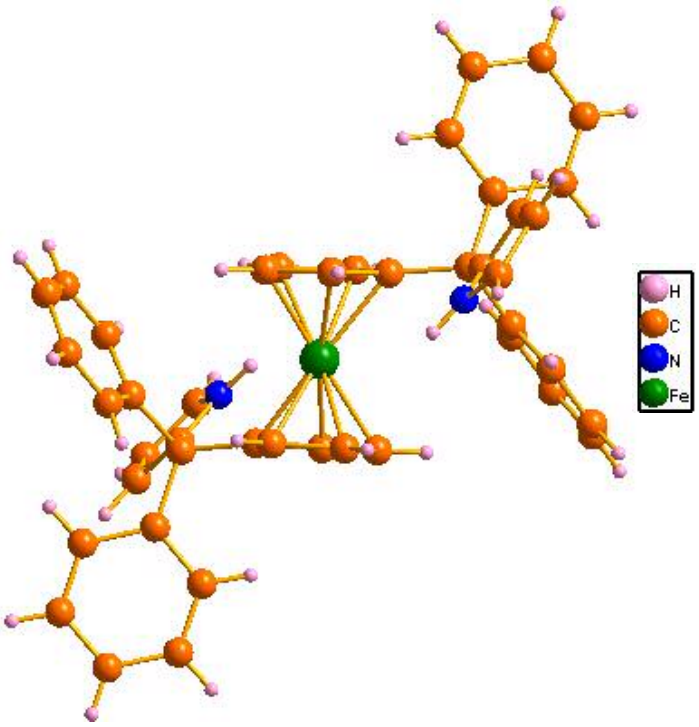


Figure – 9: Single crystal X-ray Structure of **11** (top view):

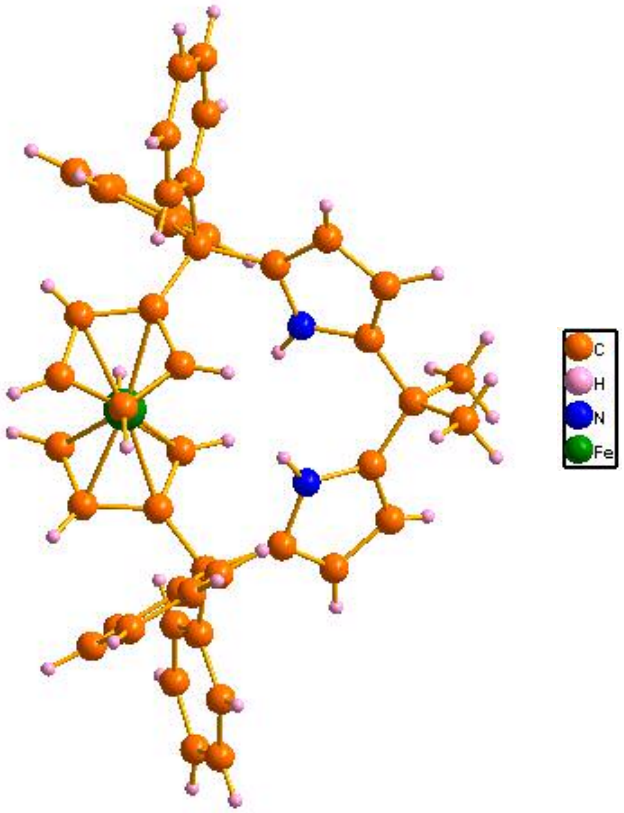
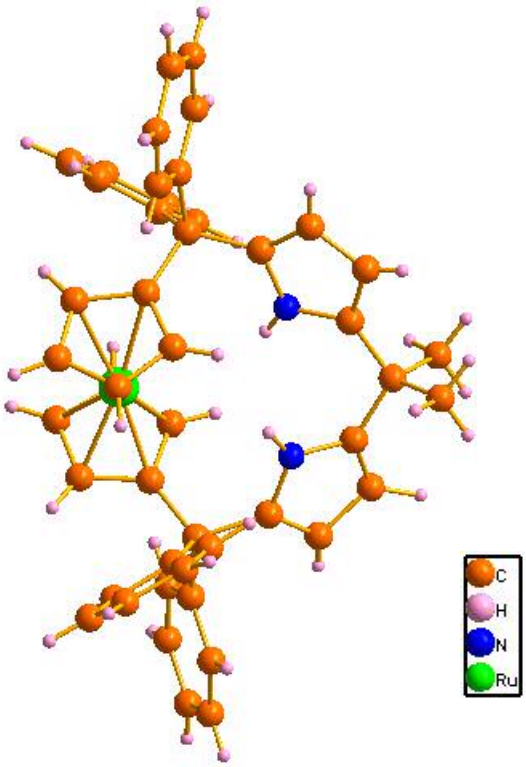


Figure – 9: Single crystal X-ray Structure of **25** (top view):



Supporting references for **6**, **11** and **25**:

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